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THE SYNTHESIS OF ALKYL KETODIHYDROQUINAZOLINS FROM ANTHRANILIC ACID.

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THEORY.

It has been shown in two previous papers[1] that the action of nitriles upon anthranilic acid, when heated together under pressure, results in the formation of ketodihydroquinazolins; and in the second paper the preparation of 2-methyl-4-ketodihydroquinazolin (or α-methyl-β-quinazolon), $C_6H_4\begin{cases}N = CCH_3\\ \quad\quad\ |\\ CO - NH\end{cases}$, was discussed in detail, both theoretically and practically. The present paper treats of the application of this method to the synthesis of higher members of the series; *viz.*, the ethyl, normal and isopropyl-, isobutyl-, and isoamylquinazalons, the last two being new; and also the preparation of several of their derivatives.

It has already been stated[2] that the addition of acetic anhydride was found very beneficial in the preparation of the methyl derivative and that the reactions thought most probable are as follows: Without anhydride:

[1] Bogert and Gotthelf: This Journal, **22**, 129 and 528.

[2] This Journal, **22**, 530.

I. $C_6H_4\begin{cases}NH_2\\COOH\end{cases} + CH_3CN = C_6H_4\begin{cases}NH_2\\CONHCOCH_3\end{cases}$

II. $C_6H_4\begin{cases}NH_2 \quad O\\CO-NH-C-CH_3\end{cases} = C_6H_4\begin{cases}N = CCH_3\\CO-NH\end{cases} + H_2O$

With anyhydride:

I. $C_6H_4\begin{cases}NH_2\\COOH\end{cases} + (CH_3CO)_2O =$

$$C_6H_4\begin{cases}NHCOCH_3\\COOH\end{cases} + CH_3COOH$$

II. $C_6H_4\begin{cases}NHCOCH_3\\COOH\end{cases} + CH_3CN = C_6H_4\begin{cases}NHCOCH_3\\CONHCOCH_3\end{cases}$

III. $C_6H_4\begin{cases}N-C-CH_3\\H\quad O\\CONH-COCH_3\end{cases} = C_6H_4\begin{cases}N = CCH_3\\CO-NH\end{cases} + CH_3COOH$

or

IV. $C_6H_4\begin{cases}N\begin{cases}H\\COCH_3\end{cases}\quad O\\CO-NH-C-CH_3\end{cases} = C_6H_4\begin{cases}N = CCH_3\\CO-NH\end{cases} + CH_3COOH$

In preparing the higher derivatives, various modifications of the process were tried in order to throw more light upon these reactions and to determine the conditions necessary for the best yield. These may be summed up as follows: Anthranilic acid was heated with:

I. Nitrile alone.

1. Propionitrile.
2. *n*-Butyronitrile.
3. Isovaleronitrile.
4. Isocapronitrile.

Nothing in confirmation of, or opposition to, the theory of this reaction as given above was discovered from these experiments. The yield varied, being very poor in some cases and good in others.

II. Nitrile and the corresponding acid anhydride.

1. Propionitrile and propionic anhydride.
2. *n*-Butyronitrile and *n*-butyric anhydride.
3. Isovaleronitrile and isovaleric anhydride.

The addition of anhydride was found to greatly increase the yield in every instance. The reaction probably taking place under these conditions has already been shown. The rapid combination of the anhydride with the anthranilic acid was indicated in each case by the mixture becoming warm and solidifying almost immediately after mixing.

The by-products of the reaction are the anilide and amide of the fatty acid whose anhydride and nitrile are used. The former is found, however, only in those tubes which show considerable pressure on opening, and its formation is, therefore, probably due to the splitting off of carbon dioxide from the acylanthranilic acid. The presence of the amide can be explained by supposing a secondary amide to form in the tube by the interaction of the fatty acid and nitrile, which then, on heating with water in the after-treatment of the tube-contents, decomposes to the primary amide:

$$RCOOH + RCN = (RCO)_2NH$$
$$(RCO)_2NH + H_2O = RCONH_2 + RCOOH$$

III. Nitrile and a different acid anhydride.

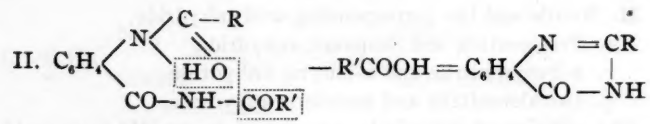
In the experiments thus far considered the formation of but one quinazolon was possible (excluding tautomeric forms), but when different anhydrides and nitriles are used, two may result, as shown by the following equations:

$$C_6H_4\begin{cases}NH_2\\COOH\end{cases} + (RCO)_2O = C_6H_4\begin{cases}NHCOR\\COOH\end{cases} + RCOOH$$

$$C_6H_4\begin{cases}NHCOR\\COOH\end{cases} + R'CN = C_6H_4\begin{cases}NHCOR\\CONHCOR'\end{cases}$$

The reaction so far is the same as usual, but now, in forming the ring, either RCOOH or R'COOH may split off, resulting in different quinazolons:

I. $$C_6H_4\begin{cases}N\begin{cases}H\\COR\end{cases}\\CONHC{=}O\\\quad\quad|\\\quad\quad R'\end{cases} - RCOOH = C_6H_4\begin{cases}N = CR'\\CO - NH\end{cases}$$



The reactions tried were:

A. Nitrile and a higher acid anhydride.

1. Acetonitrile and propionic anhydride.
2. Acetonitrile and *n*-butyric anhydride.
3. Acetonitrile and isobutyric anhydride.
4. Propionitrile and isobutyric anhydride.

In these cases the reaction always followed equation (II); *i. e.*, the anhydride determined which quinazolon was formed: (1) giving ethyl; (2) normal propyl; and (3) and (4) isopropyl quinazolon.

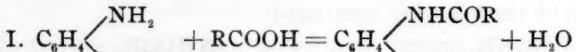
B. Nitrile and a lower acid anhydride.

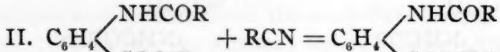
1. Propionitrile and acetic anhydride.
2. Isocapronitrile and isobutyric anhydride.
3. Isocapronitrile and *n*-butyric anhydride.

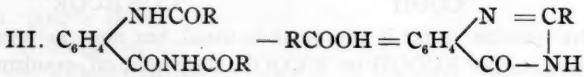
Of these, (1) yielded pure methyl quinazolon and therefore reacted according to equation (II), while (2) and (3) yielded mixtures.

IV. Nitrile and the corresponding acid.

The reaction in this case, if it follows the same course as when anhydride is used, is as follows:







It does not seem likely, however, that, especially with the higher weaker acids, reaction (I) proceeds to any great extent, if at all, as it depends on the affinity between the fatty acid and the amino group of the anthranilic acid, an affinity which, among the higher acids, is practically zero. Experiments by the writer with normal butyric and isocaproic acids show that, under the

same conditions as to heat and pressure that existed in the tubes, these acids do not combine, to any appreciable extent, with anthranilic acid.

The nitriles and acids used were :

1. Acetonitrile and acetic acid.
2. Propionitrile and propionic acid.
3. *n*-Butyronitrile and *n*-butyric acid.
4. Isocapronitrile and isocaproic acid.

In these reactions the results were very similar to those of case (II), the yields being about the same and anilides and amides being found as by-products. The formation of the amide can be more simply explained in this case by the action of the liberated water on the nitrile. In order to allow for this saponification, two molecules of nitrile were used to one each of anthranilic acid and fatty acid. The anilides are doubtless due to the action of aniline, formed by the decomposition of anthranilic acid, on either the fatty acid or the amide.

V. Nitrile and a different acid.

As in the third case, so in this one, the formation of two quinazolons is possible. The reactions tried were :

A. Nitrile and a higher acid.

1. Acetonitrile and propionic acid.
2. *n*-Butyronitrile and capric acid.
3. Isocapronitrile and capric acid.

Of these, (2) and (3) gave pure quinazolons ; the former, the normal propyl, and the latter, the isoamyl derivative. The capric acid appears, therefore, to have taken no part in the reaction, probably because it is too weak to form any acyl derivative whatever with the anthranilic acid. Reaction (1), on the contrary, gave a product which was evidently a mixture.

B. Nitrile and a lower acid.

1. Acetonitrile and formic acid.
2. Propionitrile and formic acid.
3. Isocapronitrile and formic acid.
4. Isocapronitrile and propionic acid.

Reaction (4) resulted in pure isoamyl quinazolon and (3) in isoamyl quinazolon with a trace of what appeared to be 4-ketodihydroquinazolin itself, while (1) and (2) gave, apparently, no phenmiazine derivative at all.

In considering those reactions in which anhydrides or acids not corresponding to the nitriles were used, it will be seen that their course appears to depend both on the ease with which the anhydride or acid reacts with anthranilic acid to form acylanthranilic acid, and on the molecular weights of the radicals introduced. Thus, under III, *A*, using nitrile and a higher anhydride, normal and isobutyric anhydrides were heated with acetic and propionic nitriles and in every case pure normal or isopropyl quinazolon resulted, while, under V, *A* (nitrile and a lower anhydride), the same anhydrides, when heated with isocapronitrile, yielded mixtures. Evidently, in the latter case, the superior weight of the isocaproyl radical has exerted its influence and forced out the lighter radical as indicated in equation (I).

That the product also depends upon the relative strength of the acids and anhydrides is shown by the fact that, when using anhydrides, pure quinazolons, whose formulas depended upon that of the anhydride, were obtained in five instances, while, when using acids, in every case either a mixture resulted or the quinazolon obtained depended wholely upon the nitrile used. This is clearly shown by comparing reactions III, *A*, 1 and V, *A*, 1, in which propionic anhydride and propionic acid were heated with acetonitrile and yielded, respectively, pure ethyl quinazolon and a mixture.

To roughly determine the ease with which the higher fatty acids and anhydrides combine with anthranilic acid, a few experiments were performed, a description of which will be found at the end of this paper.

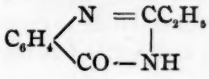
For purposes of comparison the melting-points of the quinazolons treated of in this paper are here tabulated. It will be noticed that they descend with the increase in molecular weight and that the isoderivatives melt much higher than the corresponding normal ones.

	Normal.	Iso.
Methyl	239°	....
Ethyl	234°	....
Propyl	199°–200°	230°–232°
Butyl	....	194°–195°
Amyl	....	184°

Experimental Part.[1]

In all the following work the proportions of material used, unless specially mentioned, were the same in corresponding reactions; *i. e.*, when nitrile alone was used, two molecules were heated with one molecule of anthranilic acid; when acid anhydride was added, the proportions were one molecule nitrile, one of anhydride, and one of anthranilic acid; when a fatty acid was substituted for the anhydride, one molecule of fatty acid, two of nitrile, and one of anthranilic acid were used.

2-ethyl 4-ketodihydroquinazolin.



Preparation.

I. *Anthranilic Acid and Propionitrile.*—The tube was heated to 170°–180° for six hours and then to 200°–210° for another six hours. After the first period the pressure was considerable but after the second it was slight. The tube-contents were dark-colored, completely crystalline, and smelled of ammonia. They were treated with cold sodium carbonate solution and the undissolved portion filtered out. The latter was then ground in a mortar with cold dilute caustic potash solution, the mixture filtered, the residue washed, and the quinazalon precipitated from the filtrate by passing carbon dioxide. The yield, after crystallizing once from water, amounted to 22½ per cent. of the theoretical.

The residue from the caustic potash treatment was crystallized from water and found to be propionanilide, crystallizing in leaflets, melting at 104°–105°, and yielding aniline when boiled with caustic alkali. It was probably formed by the action of aniline on propionamide, resulting in ammonia and propionanilide; as mentioned above, ammonia was found in the tube.

II. *Anthranilic Acid, Propionitrile, and Propionic Anhydride.*—This tube was heated to 160°–170° and to 200°–210° for six hours each, opening after each period. There was considerable pressure after the first heating and very little after the second, the tube contents consisting of a light brown homogeneous mass of

[1] All melting-points given, unless stated to be uncorrected, were determined with Anschütz short-scale thermometers, the entire mercury column being immersed in the heating liquid.

crystalline material. This was treated with cold sodium carbonate solution, and the residue extracted with alcohol, in which practically all dissolved. The alcoholic solution, after being decolorized with bone-black, was evaporated and the residue crystallized from water. The impure ethyl quinazolon thus obtained was separated from the propionanilide mixed with it by the use of cold dilute caustic alkali as described under (I). The yield was 31½ per cent.

With another tube the treatment with alcohol was omitted, the residue insoluble in sodium carbonate being warmed directly with dilute caustic potash for a short time. The solution was then cooled to permit the propionanilide to crystallize, filtered, and the quinazolon precipitated and purified as before. The yield in this case was 29 per cent.

The effect of an excess of anhydride and nitrile was also tried, a tube being prepared containing the substances in the proportion of 1½ molecules of anhydride and 2 of nitrile to 1 molecule of anthranilic acid. It was heated to 160°–170° for six hours and to 200°–210° for a similar period and yielded 30 per cent. of quinazolon.

III. *Anthranilic Acid, Propionitrile, and Propionic Acid.*—A tube containing these was heated to 160°–165° and to 200°–210° for five hours each. There was strong pressure after the first heating but little after the second, and the contents were light-colored and crystalline. They were treated successively with sodium carbonate and caustic potash solutions in the manner already described and the yield was 36 per cent. of the theoretical. Propionanilide was again a by-product.

Another tube containing the same amounts of material was heated to 150°–160° for five hours and to 175°–180° for five hours. The contents, after treatment with soda solution, were crystallized directly from water and yielded 28 per cent. of quinazolon.

IV. *Anthranilic Acid, Acetonitrile, and Propionic Anhydride.*—The tube was heated successively to 180°–190°, 220°–230°, and 225°–235° for five hours each. The pressure at any time was slight. After washing with soda solution the product was crystallized from water and a yield of about 17 per cent. of ethyl quinazolon obtained. No methyl quinazolon could be found although the experiment was repeated several times and the by-products carefully examined.

Properties.

The ethyl quinazolon obtained by the above methods agreed in all its properties with those observed by Bischler and Lang[1] and by Niementowski.[2] It crystallizes from water in long fine needles which are moderately soluble in hot water, slightly in cold, easily in alcohol and benzene. Its melting-point is given by Bischler and Lang as 227°–228° and by Niementowski as 225°. The writer found 227°–228° to be the uncorrected melting-point and 234° the corrected.

Derivatives.

Methyl Ether, $C_6H_4\begin{cases} N = C - C_2H_5 \\ \quad\quad\quad | \\ CO - N - CH_3 \end{cases}$.—This is prepared by heating the quinazolon with caustic alkali and methyl iodide in alcoholic solution, for a few hours, with a return condenser, evaporating the alcohol and treating the residue with water. Sometimes the addition of a little more caustic alkali is necessary at this point to cause the complete separation of the ether, which is then filtered out and crystallized from water. It forms long colorless needles melting at 121°.

Hydrochloride.—This salt results from the action of hydrochloric acid on the quinazolon. It crystallizes in needles which sublime without melting.

Nitrate.—The nitrate crystallizes from a hot solution of the base in nitric acid (1 : 4) in the form of coarse yellow needles which melt with decomposition at 173°–174°.

Sulphate.—This salt is obtained by saturating cold dilute sulphuric acid with quinazolon, filtering and concentrating the filtrate. It forms coarse needles which gradually darken on heating and melt at 240°–241°.

Chromate.—The chromate crystallizes from a hot concentrated aqueous solution of quinazolon and chromic acid, in the form of light brown needles which decompose at about 155°.

Picrate.—This is prepared in the same way as the chromate but is less soluble in cold water. It crystallizes in thin plates of a light yellow color and melts at 191°–192°.

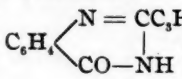
[1] *Ber. d. chem. Ges.*, **28**, 280.
[2] *J. prakt. Chem.*, (2), **51**, 564.

Oxalate.—This is also prepared as is the chromate and forms long needles melting at 180–181°.

Chlorplatinate.—The quinazolon is dissolved in hot hydrochloric acid and an excess of platinic chloride added; on cooling, the double salt separates as a red crystalline powder. It was analyzed for platinum with the following results:

	Calculated for $(C_{10}H_{10}N_2O.HCl)_2PtCl_4$.	Found. I.	II.
Platinum.....	25.63	25.66	25.63

2-*n*-PROPYL 4-KETODIHYDROQUINAZOLIN.



Preparation.

I. *Anthranilic Acid and n-Butyronitrile.*—The tube was heated to 120°–125° for four and one-half hours, 200°–210° for six hours, and 210°–220° for six hours, opening after each period. The pressure was considerable only after the second period and the product was crystalline. After the usual sodium carbonate treatment the residue was crystallized from water. The quinazolon thus obtained was dissolved in cold caustic alkali to separate it from *n*-butyranilide but none of the latter was found. The base was then precipitated with carbon dioxide as usual and crystallized from water. The yield was about 17 per cent.

The sodium carbonate solution used in the first treatment was evaporated, the residue extracted with ether, and the extract crystallized from benzene. Leaflets were obtained melting at 112°–113°, very soluble in water, and evolving ammonia when boiled with caustic alkali. Hofmann[1] states that *n*-butyramide melts at 115°.

II. *Anthranilic Acid, n-Butyronitrile, and n-Butyric Anhydride.*—A tube containing these substances was heated to 180°–190° for four hours and to 190°–200° for five hours. The yield was 30 per cent. Another tube heated to 180°–190° for five and one-half hours and to 210°–220° for six hours gave 39 per cent.

There was practically no pressure in either case and the contents were very light-colored. Both products were treated in the same way; first washed with sodium carbonate solution and then twice crystallized from water, decolorizing with bone-black.

[1] *Ber. d. chem. Ges.*, **15**, 982.

The soda solutions were found to contain *n*-butyramide as in the last case.

No butyranilide was found and none was expected from the fact that the slight pressure in the tubes showed that practically no anthranilic acid had decomposed.

III. *Anthranilic Acid, Acetonitrile, and n-Butyric Anhydride.*—The tube was heated to 180°–190° for five hours and to 210°–220° for six hours. There was no pressure. The contents were treated as in (II). The quinazolon obtained agreed in all its properties with *n*-propylquinazolon. The yield was about 28 per cent.

By evaporating the soda solution, extracting the residue with ether, and crystallizing the extract from benzene, a very small amount of material was obtained which softened at 93°, but was not entirely melted at 130°. It dissolved completely in cold dilute caustic potash and was reobtained by passing carbon dioxide and concentrating the solution. On crystallizing from benzene it now melted at 232°–233° (uncorrected), and was probably methyl quinazolon.

IV. *Anthranilic Acid, n-Butyronitrile, and n-Butyric Acid.*—The tube was heated for three periods of six hours each to 165°–175°, 210°–215°, and 230°–240°. After each of the first two periods there was considerable pressure, but after the third, there was none. The product was treated successively with soda solution and dilute caustic alkali, and the quinazolon precipitated from the latter solution as usual by passing carbon dioxide. It was purified by crystallization from water.

The part insoluble in the caustic alkali was found, on recrystallizing from dilute alcohol, to be *n*-butyranilide. It melted at 93°–94° and yielded aniline when boiled with concentrated alkali. Gerhardt[1] gives the melting-point of *n*-butyranilide as 90° but the writer found that anilide prepared by boiling *n*-butyric acid with aniline for a few hours, pouring the product into water, and crystallizing the precipitate from dilute alcohol, melted at 93°–94°, and otherwise agreed with that obtained from the tube.

The soda solution, as usual, contained *n*-butyramide.

Properties.

Normal propyl quinazolon has been prepared by Bischler and Lang,[2] who found the melting-point to be 205°. While in all

[1] *Ann. Chem.* (Liebig), **87**, 166.
[2] *Ber. d. chem. Ges.*, **28**, 286.

other properties the quinazolon obtained by the writer agrees with that of these authors, its melting-point is 199°–200°.

Derivatives.

The salts and ethers of this and the following quinazolons were almost all prepared in exactly the same way as were those of ethyl quinazolon and therefore only their properties are given.

Methyl ether, $C_6H_4\begin{cases}N = C - C_3H_7\\ \quad\quad\quad |\\ CO - N - CH_3\end{cases}$, crystallizes from water in long colorless needles melting at 77°–78°.

Hydrochloride.—Thin plates which sublime without melting.

Nitrate.—Coarse flat needles melting with decomposition at 159°–160°.

Sulphate.—Long coarse needles melting at 227°–228°.

Chromate.—Yellow crystalline powder. On heating, it gradually darkens, commencing at about 150°.

Picrate.—Light yellow needles with serrated edges, melting at 183°–184°.

Oxalate.—White needles melting at 193°–194°.

Chlorplatinate.—Coarse red crystals. The platinum was determined by ignition.

	Calculated for $(C_{11}H_{12}N_2O.HCl)_2PtCl_4$.	Found. I.	II.
Platinum	24.71	24.79	24.82

2-ISOPROPYL 4-KETODIHYDROQUINAZOLIN.

$$C_6H_4\begin{cases}N = CCH(CH_3)_2\\ \quad\quad\quad |\\ CO - NH\end{cases}$$

No isobutyric nitrile being conveniently at hand, its action alone on anthranilic acid could not be studied. It was found, however, that, for the production of isopropyl quinazolon, the use of isobutyric nitrile was unnecessary, and that the combined action of isobutyric anhydride and a lower nitrile, acetic or propionic, on anthranilic acid resulted in its formation, the yield, especially with propionitrile, being very good.

I. *Anthranilic Acid, Isobutyric Anhydride, and Propionitrile.*—The tube was heated to 180°–190° for five hours, 210°–220° for five hours, and 230°–240° for twelve hours. The pressure at any time was very slight. After preliminary treatment with sodium

carbonate solution the product was crystallized from alcohol and decolorized with bone-black. The yield of quinazolon was about 40 per cent.

Another tube was heated to 180°–190° for six hours and to 210° for six hours and yielded 32 per cent.

No trace of ethyl quinazolon was found in either of these tubes.

II. *Anthranilic Acid, Isobutyric Anhydride, and Acetonitrile.*—This tube was heated to 180°–190° for five hours and 210°–220° for six hours and yielded 15½ per cent. of isopropyl quinazolon, the process of purification being the same as when using propionitrile.

Properties.

Bischler and Lang[1] and Niementowski[2] have prepared isopropyl quinazolon but differ as to its melting-point, the former giving it as 195°–196° and the latter as 224°. Niementowski[3] has suggested that this difference may be due to a difference in constitution in the sense of tautomerism.

The quinazolon obtained by the writer melts at 225°–226° uncorrected or at 231°–232° corrected; it therefore agrees quite well with Niementowski's product. Its other properties are the same as those recorded by these authors.

A peculiarity in the solubility of this base was observed by the writer, which possibly indicates that it consists of a mixture of the two forms, keto and hydroxy? While all the other quinazolons, when in a fluffy crystalline condition, dissolved instantly in cold dilute caustic alkali, it was found that the isopropyl showed a difference in the rapidity of solution. Only a portion dissolved instantly; the rest remained undissolved for a short time, though it ultimately also went into solution. In one case the slower dissolving portion was filtered out, washed, and dried. Its melting-point was found to be 223°, while the portion which had dissolved, when precipitated with carbon dioxide and crystallized from alcohol, melted at 231°–232°, the ordinary melting-point of the quinazolon. No further work has, at present, been done on this subject.

[1] *Ber. d chem. Ges.*, **28**, 287.
[2] *J. prakt. Chem.* (2), **51**, 569.
[3] *Ber. d. chem. Ges.*, **27**, R., 516.

Derivatives.

Methyl Ether, $C_6H_4\begin{cases}N=C-C_3H_7\\ \quad\quad|\\ CO-N-CH_3\end{cases}$.—Long silky needles melting at 78°–79°.

Hydrochloride.—Rectangular plates.

Sulphate.—Coarse needles melting at 219°–220°.

Chromate.—Transparent coarse brown needles which decompose on heating.

Picrate.—Light yellow crystalline powder melting at 213°–214°.

Chlorplatinate.—Coarse red crystals. The platinum was determined by ignition.

	Calculated for $(C_{11}H_{12}N_2O.HCl)_2PtCl_4$.	Found. I.	II.
Platinum.....	24.71	24.85	24.69

2-ISOBUTYL 4-KETODIHYDROQUINAZOLIN.

$$C_6H_4\begin{cases}N=CC_4H_9\\ \quad\quad|\\ CO-NH\end{cases}$$

Preparation.

I. *Anthranilic Acid and Isovaleronitrile.*—The tube was heated to 160°–165° for five hours and to 200°–210° for five hours. Moderate pressure was found on opening, and the contents were dark-colored but crystalline. They were heated with dilute caustic potash solution for a short time, the solution cooled, filtered, and carbon dioxide passed into the filtrate. The precipitated quinazolon was then crystallized from water. The yield was only 5 per cent. of the theoretical.

II. *Anthranilic Acid, Isovaleronitrile, and Isovaleric Anhydride.*—The mixture was heated successively to 180°–190° for five hours, 210°–220° for five hours, and 230°–240° for twelve hours. The pressure in the tube was very slight and the contents were light-colored and entirely crystalline. They were treated with soda solution and then crystallized from dilute alcohol. To separate the quinazolon from isovaleranilide the treatment with cold dilute caustic alkali was applied to this product. The anilide was crystallized from dilute alcohol and obtained in the form of colorless needles melting at 112°–113°, and yielding aniline when boiled with concentrated alkali. The quinazolon, after precipita-

tion with carbon dioxide, was crystallized from water and amounted to 35 per cent. of the theoretical yield.

The soda solution with which the tube-contents were first treated was evaporated and the residue extracted with ether. The extract was crystallized from benzene and found to be isovaleramide melting at 131°, and evolving ammonia when boiled with alkali.

Another tube containing the same materials and heated to 190°–200° for three hours and to 225° for six hours yielded 26 per cent.

Properties.

Isobutyl quinazolon crystallizes from water in small needles melting at 194°–195°. It is moderately soluble in hot water, very slightly in cold, somewhat in ether, and easily soluble in alcohol and hot benzene.

Derivatives.

Methyl Ether, $C_6H_4\begin{cases}N=C-C_4H_7\\ \quad\quad|\\ CO-N-CH_3\end{cases}$.—Colorless needles melting at 68°–69°.

Hydrochloride.—Coarse needles.

Nitrate.—Yellow plates decomposing at 171°–172°.

Sulphate.—Needles arranged in bunches and melting at 228°–229°.

Chromate.—Yellow crystalline powder which decomposes at 154°.

Picrate.—Light yellow needles melting at 192°.

Oxalate.—White felted needles melting at 204°–205°.

Chlorplatinate.—Transparent coarse brown needles. It was analyzed for platinum.

	Calculated for $(C_{12}H_{14}N_2O.HCl)_2PtCl_4$.	Found. I.	II.
Platinum	23.86	23.93	24.00

2-ISOAMYL 4-KETODIHYDROQUINAZOLIN.

$$C_6H_4\begin{cases}N=CC_5H_{11}\\ \quad\quad|\\ CO-NH\end{cases}$$

Preparation.

I. *Anthranilic Acid and Isocapronitrile.*—The tube was heated to 180–185° for five hours, to 220–225° for six hours, and to 240°–

250° for six hours. Moderate pressure was found after the first period but none after the second and third. The quinazolon was extracted and purified exactly as was isobutyl quinazolon (I). The yield was 18 per cent.

II. *Anthranilic Acid, Isocapronitrile, and Isocaproic Acid.*—This tube was heated successively to 185°–190°, 210°–215°, and 230°–240° for six hours each. Considerable pressure was found only after the first heating. The product was treated in exactly the same way as was that of the isobutyl tubes (II). The yield of quinazolon was 37 per cent.

An anilide was found as usual. It crystallized from dilute alcohol in long needles melting at 110°–111°, and yielding aniline when boiled with alkali.

0.1533 gram gave 9.9 cc. nitrogen (20°, 761 mm.).

	Calculated for $C_{12}H_{17}NO$.	Found.
Nitrogen	7.33	7.39

It is therefore, as was expected, isocaproanilide. As the properties of this anilide have apparently not been recorded, some was prepared by boiling isocaproic acid with aniline for a short time, pouring the product into water, and crystallizing the precipitate from dilute alcohol. Its properties were found identical with those of the anilide obtained from the tube.

0.1814 gram gave 11.9 cc. nitrogen (21°, 762 mm.).

	Calculated for $C_{12}H_{17}NO$.	Found.
Nitrogen	7.33	7.49

Another by-product found in this tube was isocaproamide, extracted from the sodium carbonate solution by the usual method. It melted at 119°–120° and evolved ammonia when boiled with alkali.

Properties.

Isoamyl quinazolon crystallizes from water in very small felted needles melting at 184°. It is soluble in ether, alcohol, and benzene, moderately in boiling water and almost insoluble in cold. The nitrogen was determined with the following results:

I. 0.1563 gram gave 18.3 cc. nitrogen (23°, 752 mm.).
II. 0.1494 gram gave 17.3 cc. nitrogen (22°, 753 mm.).

	Calculated for $C_{13}H_{16}N_2O$.	Found. I.	Found. II.
Nitrogen	12.96	13.05	13.02

Derivatives.

Methyl Ether, $C_6H_4\begin{cases}N = C - C_5H_{11}\\ CO - N - CH_3\end{cases}$.—This ether is more difficult to obtain crystalline than is that of any of the other quinazolons. It was prepared in the usual way by heating the quinazolon with methyl iodide and caustic alkali in alcoholic solution. The alcohol was evaporated, the residue taken up with water, and extracted with ether. The ether solution was evaporated and the methyl ether obtained in the form of an oil, which solidified only after long standing in a desiccator. To obtain it in crystals various solvents were tried, but without success. The method finally used was to form the hydrochloric acid salt, dissolve it in water, add a slight excess of sodium carbonate, while cooling with ice, and finally inoculating the milky solution with some of the solid ether obtained in the desiccator. On standing, crystals finally appeared in the form of small needles melting at 40°–41°, and practically insoluble in water.

Hydrochloride.—Fine needles.

Nitrate.—Thin plates decomposing at 160°–161°.

Chromate.—Attempts to prepare this salt were unsuccessful. The methods used were the action of chromic acid on the base and double decomposition between the hydrochloride of the base, and potassium chromate. In neither case was any crystalline product obtained, the base apparently decomposing.

Picrate.—Yellow leaflets melting at 164°–165°.

Chlorplatinate.—This salt could not be obtained, the affinity between the hydrochloride of the base and platinic chloride seeming to be very weak.

In general it appears that the salts of the higher quinazolons are weaker and more easily dissociated than are those of the lower.

MISCELLANEOUS REACTIONS.[1]

Nitrile and a Lower Acid Anhydride.

I. *Anthranilic Acid, Propionitrile, and Acetic Anhydride.*—The tube was heated to 140°–150° for three hours, 180°–190° for five hours, and 200°–205° for six hours. There was practically no

[1] The order and numbering of these reactions are the same as in the first part of the paper.

pressure at any time and the contents were completely crystalline. After washing with sodium carbonate solution, the product was extracted with boiling water. From this solution, on cooling, methyl quinazolon separated in considerable quantity. The residue, after the water extraction, was a brown amorphous powder from which nothing crystalline could be obtained.

The methyl quinazolon was identified by its melting-point, physical properties, and by the melting-point of its methyl ether.

No ethyl quinazolon was found.

II. *Anthranilic Acid, Isocapronitrile, and Isobutyric Anhydride.*—The mixture was heated to 210°–220° for five and one-half hours. The pressure, on opening, was slight and the contents were light-colored and crystalline. After preliminary treatment with sodium carbonate, the caustic alkali method of extraction was applied to the residue.

The quinazolon so obtained melted gradually from 200°–205°, and, when sublimed, these limits were increased to 180°–210°, while the melting-points of the two possible products, isopropyl and isoamyl quinazolons are, respectively, 225°–226° and 179°–180° (uncorrected). Recrystallization three times from water did not appreciably change this point. Three crystallizations from alcohol were necessary to obtain pure isopropyl quinazolon melting at 226°–227° (uncorrected). A system of fractional crystallization was applied to the mother-liquor but no product was obtained melting wholly below 205°, although several began to melt around 190°.

That this product and those obtained from some of the reactions still to be described are mixtures seems certain when it is considered that in all other cases the quinazolons were obtained pure after the caustic alkali treatment and one crystallization, and that, as the reactions proceeded just as smoothly, it is unlikely that any exceptional impurities were formed. The difficulty in separating the mixtures is due to the great similarity in the properties of their constituents; the successful identification of isopropyl quinazolon in the reaction just described is due to its slightly smaller solubility in alcohol as compared with isoamyl quinazolon; it was also undoubtedly present in the larger quantity.

III. *Anthranilic Acid, Isocapronitrile, and n-Butyric Anhydride.*—Heated to 180°–185° for five hours, 220°–225° for six hours, and

240°–250° for six hours. The pressure was very slight at any time and the contents crystalline. The soda and caustic alkali method of purification was used. The quinazolon obtained melted at 187°–188°, and, on recrystallization, at 184°–187°. The two quinazolons which it was possible to have formed in this reaction, the normal propyl and the isoamyl, melt respectively at 194°–195° and 179°–180° (uncorrected).

As the methyl ether of the normal propyl quinazolon is quite soluble in hot water while that of the isoamyl is almost insoluble, it was thought that this might prove a method of separation. Only the ether of normal propyl quinazolon could, however, be identified; but, on account of the small amount of material available and the difficulty experienced in getting isoamyl quinazolon methyl ether crystalline, as already mentioned, this can hardly be considered a proof that none of that base was present.

Nitrile and a Higher Acid.

I. *Anthranilic Acid, Acetonitrile, and Propionic Acid.*—The tube was heated to 170°–180° for five hours. On opening, a moderate pressure was observed. The contents were treated exactly as in the last reaction. The quinazolon obtained melted at 213°–214° (uncorrected), and this point remained constant on sublimation. Recrystallization from water raised it to 218°–220°, and this also did not change on sublimation. Methyl and ethyl quinazolons melt, respectively, at 232° and 227°–228° (uncorrected), while their methyl ethers melt at 110°–111° and 121°–122° (uncorrected). The methyl ether obtained from the supposed mixture melted indefinitely at from 90°–105°.

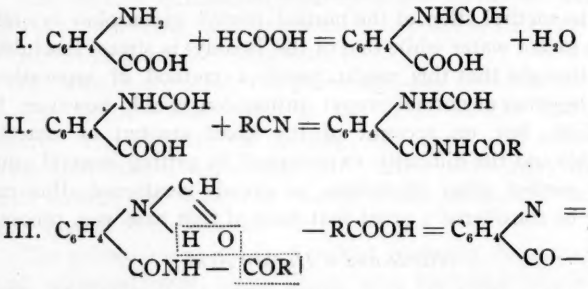
II. *Anthranilic Acid, n-Butyronitrile, and Capric Acid.*—The mixture was heated to 185° for six hours and to 200°–210° for five and one-half hours. The pressure was moderate and the tube-contents light in color and crystalline. The quinazolon was separated and purified as in the last case and was found to be the pure normal propyl derivative melting at 199°.

III. *Anthranilic Acid, Isocapronitrile, and Capric Acid.*—The tube was heated exactly as was No. 2. After the first period the pressure was moderate and the contents consisted almost entirely of a dark red liquid with a very small amount of solid matter; after the second period, however, they were wholly crystalline. By following the same method of separation as in No. 2 and crys-

tallizing the product from dilute alcohol, pure isoamyl quinazolon, melting at 184°, was obtained.

Nitrile and a Lower Acid.

The following experiments of heating anthranilic acid with formic acid and various nitriles were performed in the hope of obtaining 4-ketodihydroquinazolin itself, as follows:



In the other experiments on the action of acids and nitriles on anthranilic acid it was found that, apparently, the question as to whether a single or a mixture of quinazolons will form depends on the ease with which the fatty acid combines with the anthranilic acid to form an acylanthranilic acid; it was thought, therefore, that, as formic and anthranilic acids react with the greatest ease, the above reaction was a very likely one. On trial, however, it was found that while formylanthranilic acid is quickly formed it apparently does not react with nitriles at temperatures at which it is stable; according to Meyer and Bellmann,[1] formylanthranilic acid, when heated with water, decomposes at 130°–140° into formic acid, carbon dioxide, and aniline.

I. *Anthranilic Acid, Formic Acid, and Acetonitrile.*—One tube containing these was heated to 100°–110° for twelve hours. There was no pressure and the contents were completely crystalline. On adding sodium carbonate solution the entire product dissolved, showing that no quinazolon was present. The addition of hydrochloric acid to the solution caused a precipitate, which, washed and crystallized from water, was found to be formylanthranilic acid, melting at 165°–166°.

Another tube was heated to 100°, 140°–150°, and 190°–200° for six hours each. After the first period there was no pressure and

[1] *J. prakt. Chem.*, (2), **33**, 25.

the contents were crystalline and much as in the first tube; after the second, the pressure was moderate and the contents were entirely liquid; after the third, there was again moderate pressure and the contents consisted of about half crystals and half liquid. The treatment with sodium carbonate followed by dilute caustic alkali was applied, but, on passing carbon dioxide into the alkali solution, the precipitate obtained was so slight that nothing further was done with it.

II. *Anthranilic Acid, Formic Acid, and Propionitrile.*—The results from this reaction were as unsatisfactory as those just detailed.

III. *Anthranilic Acid, Formic Acid, and Isocapronitrile.*—This tube was heated to 120°–125° for five hours, 160°–170° for six hours, and 210°–220° for six hours. There was considerable pressure and the product consisted of a sirupy liquid and a small amount of crystalline material. The same treatment as in the previous tubes was used and a small amount of isoamyl quinazolon obtained.

The sodium carbonate solution was evaporated, the residue extracted with ether, and the extract crystallized from benzene. Two kinds of crystals were obtained and these were separated by treatment with warm benzene, which dissolved one faster than the other. The more soluble substance was found to be isocaproamide, melting at 119°–120°, while the less soluble one, melting at 190°–195°, and, on sublimation, at 211° (uncorrected), was probably 4-ketodihydroquinazolin. The melting-point of this quinazolon is stated by Knape[1] to be 211°–212° and by Bischler and Burkart[2] to be 209°.

As it has been shown that the best yields of quinazolon were obtained when using the nitrile and the corresponding acid or anhydride, the correct nitrile to use with formic acid, for the production of 4-ketodihydroquinazolin, is formic nitrile or hydrocyanic acid. No anhydrous hydrocyanic acid being available, a few experiments were tried aiming to produce the acid in the tube as the reaction proceeded, but no encouraging results were obtained.

IV. *Anthranilic Acid, Isocapronitrile, and Propionic Acid.*—The mixture was heated to 170°–180° for five hours and then to 200°–

[1] *J. prakt. Chem.*, (2), **43**, 214.
[2] *Ber. d. chem. Ges.*, **26**, 1349.

210° for six hours. There was considerable pressure after the first period but none after the second. The contents were almost wholly crystalline. The quinazolon was extracted and purified by the same method as followed above, and proved to be the isoamyl derivative. Its melting-point was 183°–184°.

Action of Fatty Acids and Anhydrides on Anthranilic Acid.

These experiments were performed for the purpose already stated on page 614. Anthranilic acid was heated with normal butyric and isocaproic acids respectively, both in sealed tubes and open, at temperatures varying from but slightly above 100° to the boiling-point of the fatty acid, without any action being discernible. In contradistinction to this it was found that both normal butyric and isovaleric anhydrides reacted quite smoothly to form the corresponding acylanthranilic acids. Merely heating the acid and anhydride together on the water-bath for three to four hours was sufficient to give a yield of about 30 per cent.

Only the isovalerylanthranilic acid was closely examined. It crystallizes from water in needles melting at 110°–111°.

I. 0.1816 gram gave 10.6 cc. nitrogen (26°, 755 mm.).

II. 0.2016 gram gave 11.7 cc. nitrogen (23°, 754 mm.).

	Calculated for $C_{12}H_{15}NO_3$.	Found. I.	II.
Nitrogen.....	6.33	6.43	6.49

This work is being continued and extended, and other papers will appear shortly.

ORGANIC LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY, June 1, 1901.

ON THE ESTIMATION OF UREA IN URINE.

BY J. H. LONG.

Received July 23, 1901.

INASMUCH as about 90 per cent. of the total assimilated nitrogen leaving the human body is excreted in the form of urea the accurate determination of this substance in the urine must remain among the most important of physiological-chemical problems. The interest attaching to the question is fully shown by the great number of contributions to the subject appearing in the chemical literature, yet, notwithstanding all that has been written, the problem is still far from satisfactory solution. In the older text-books of urine analysis the Liebig method by use of mercuric

nitrate held long the first place, which was later taken by that of Knop and Hüfner, depending on the reaction between a hypochlorite or hypobromite and urea.

The original Liebig method was found to give results which were too high because of the precipitation of other substances than urea by the mercuric nitrate, and as the extent of the possible error here became more and more apparent, the method fell into disfavor and was finally practically discarded. In the later editions of the well-known manual of urine analysis by Neubauer and Vogel, revised by Huppert, the Liebig process is no longer described among the quantitative methods.

The fate of the hypobromite processes, as scientific methods, is almost as interesting. In these, plus and minus errors were long supposed to nearly balance each other. A part of the urea fails to decompose according to the simple reaction,

$$CON_2H_4 + 3NaOBr = 3NaBr + CO_2 + N_2 + 2H_2O,$$

while, on the other hand, many other nitrogenous bodies in the urine give up a large but variable part of their nitrogen in the free form under the influence of the same reagent. The modifications of this general method are almost beyond number, but in the final results there is probably even less constancy than in the older mercury method. In the editions of the Neubauer and Vogel work referred to above the Knop-Hüfner method is described only among the qualitative reactions.

From the standpoint of those interested in the practical determination of urea this omission must be looked upon as a mistake since the supposedly more accurate processes which are now described are not at all suited for quick comparative determinations in cases where many tests have to be made. It is possible that the mercury method, under special circumstances, may still render service here, and it is the object of this communication to point out how certain corrections may be applied, where comparatively full analyses are being made, with fresh urine.

The main sources of error in titrations of urea in urine by the standard solution of mercuric nitrate are these:

a. The chloride present retards the reaction, but as this effect has long been accurately known and easily corrected it will not be discussed in this place.

b. Ammonia which is always normally present, even in fresh

urine, combines likewise with the mercury solution, and prevents precipitation until a certain excess of the latter is added.

c. Uric acid, which amounts to 800 mg., or more sometimes, in the day's urine combines with the reagent to form a definite compound. The effect of this is, however, relatively small.

d. Creatinin, after urea the most abundant of the nitrogenous urinary products, forms several crystalline combinations with mercuric nitrate. The composition of these is variable with the concentration of the reacting solutions, but in any event the error in the titration of the urea in presence of this body is quite appreciable.

e. In addition to the above, several other nitrogenous compounds, present in small amount in the urine, are known to combine with mercuric nitrate, but their effect is extremely small and may usually be neglected.

I have undertaken to estimate the effect of the main disturbing factors referred to and present below some experimental data.

AMMONIA.

In fresh normal urine the amount of ammonia present is about 600 mg. for each 1000 cc. of excretion. In urine which is allowed to stand, the amount rapidly increases from decomposition of the urea. To determine the influence of this small weight of ammonia in urea titrations, tests were carried out on solutions containing ammonia alone, in the form of nitrate, and on solutions containing ammonia and urea. The ammonia was used in the form of nitrate because in the usual method of preparing urine for titration it would be left in that combination.

Experiment 1.—A solution was made which contained in 500 cc. 2.5 grams of pure ammonium nitrate. This corresponds to 1.06 gram of NH_3 to the liter; 20 cc. of this solution were measured into a beaker and standard mercuric nitrate solution added. No precipitate appeared but at the same time no reaction immediately followed on bringing a drop of the liquid in the beaker in contact with a paste of sodium bicarbonate and water. It was found that about 2.5 cc. of the usual standard mercuric nitrate solution must be used before a reaction appeared, indicating the presence of an excess of the mercury. Neutralization of the liquid in the beaker with sodium carbonate made no appreciable difference in the result.

Experiment 2.—Tests were made with a weaker ammonia solution containing 0.6 gram to the liter. The results were nearly the same as before, the volume of the mercury solution required being, however, relatively a little greater. As the end reaction is by no means as sharp as with pure urea solutions it is easy to pass the right end-point in titration. Many single titrations were made and as a mean of the closely agreeing results it may be said that with the solutions used, 20 mg. $NH_3 = 2.5$ cc. of the mercury solution.

This corresponds to 17 NH_3 to 2.12 cc. mercury solution, 17 NH_3 to 164 mg. HgO, 1 mol. NH_3 to 0.75 mol. HgO, or 4 NH_3 to 3 HgO, approximately.

Experiment 3.—Here solutions containing both urea and ammonia were titrated. The urea solution used contained exactly 2 grams in 100 cc. In a series of experiments it was found that mixtures containing 10 cc. of this urea solution, and 10 cc. of the first described ammonia solution required 21.6 cc. of the mercury solution instead of 20 cc. This makes the effect of the ammonia a little greater than in the above experiments, 1 and 2. But as intimated, the reaction is not as clear as in absence of ammonia, and a trifling excess must always be added from the mercuric nitrate burette. The end-point seems to vary also slightly with the temperature.

As a mean result the presence of 10 mg. of ammonia in the 20 cc. of mixed liquid titrated increases the amount of mercury solution used by about 1.6 cc. This corresponds closely to 1 cc. of the mercury solution for 6 mg. of ammonia, and this is the average amount present in 10 cc. of urine, the volume usually taken for titration; this is much lower than is a result given by Feder[1] according to whom 10 mg. of ammonia require 2.6 cc. of the mercury solution. This result is probably too high, and was not approached in any one of the numerous single titrations I made.

URIC ACID.

The amount of uric acid in the urine was formerly much underestimated, but since the introduction of better methods of determination higher, and probably pretty accurate, results may be easily obtained. In a large number of urines studied in this laboratory, the uric acid has been found to amount to about 650 mg.

[1] See Neubauer and Vogel; "Urine Analysis," 8th German Edition, p. 272.

for 1000 cc. of urine. In 10 cc. of urine we have therefore about 6.5 mg. of uric acid normally, and it is the interference of this that we have to consider in the urea titration. For the experiments I made up a test solution containing 250 mg. of pure uric acid dissolved by the aid of a little alkali to make 250 cc. The behavior of this with the mercury solution is regular and the same slight increase is found whether we use the simple uric acid solution or one containing uric acid and urea.

For a solution containing in 20 cc. 200 mg. of urea, and 5 mg. of uric acid the amount of mercury solution required was just 0.1 cc. more than for the urea solution alone, and by increasing the uric acid the increase in the required mercuric nitrate was found to be in the same proportion. The correction for the presence of uric acid is therefore very small, and in any case would not exceed 0.15 cc. of the mercury solution for the volume of 10 cc. of urine ordinarily taken for the titration.

CREATININ.

This is present in urine to the extent of 1 gram to 1.6 grams or more in the volume of 1000 cc. In a large number of tests I found an average of 1.4 grams by the method of precipitation with zinc chloride. On this basis 10 cc. of urine would contain 14 mg. of creatinin.

To study the behavior of this body I first prepared it in pure condition from urine by decomposing the zinc chloride precipitate with lead hydroxide. Later much larger quantities were made by separating first pure creatin from extract of beef and then decomposing the product obtained by long heating of this with strong hydrochloric or 25 per cent. sulphuric acid, by means of lead hydroxide or barium carbonate.

As was long ago pointed out by Neubauer[1] mercuric nitrate added to a creatinin solution produces no immediate precipitate; a combination is formed in which acid is liberated and this interferes with precipitation. On neutralizing the liquid with sodium carbonate a point is reached, however, when a precipitate soon forms and settles out. Under certain conditions a precipitate with the composition $(C_4H_7N_3O)_2Hg(NO_3)_2HgO$ may be obtained in this way. But with variations in the concentration of the reacting bodies the composition of the precipitate varies, as I have found by experiment. In the titration of weak creatinin solutions

[1] See Neubauer and Vogel: "Urine Analysis."

similar results are found; the solution must be neutralized with sodium carbonate to secure precipitation. In tests made I employed a creatinin solution containing 1 gram in 100 cc.

Experiment 1.—Of this solution I took 10 cc. and added nearly 5 cc. of the mercuric nitrate solution before any appreciable reaction appeared, on testing as usual with sodium bicarbonate. The solution in the beaker was still quite clear; a little methyl orange was added and then 3 cc. of normal sodium carbonate solution to change of color. This is a rough measure of the liberated acid.

Experiment 2.—In a second experiment with 20 cc. of the creatinin solution, 9 cc. of the mercuric nitrate were added before securing a trace of a reaction in the sodium bicarbonate. With 10 cc. of the mercury solution the reaction was sharp and 1 cc. of normal sodium carbonate was added to produce haziness in the liquid in the beaker. It appears, therefore, that about 9.5 cc. of the standard mercuric nitrate solution may be taken as equivalent to 20 cc. of the creatinin solution. For this concentration this corresponds very closely to a relation of 1 molecule of creatinin to 2 molecules of mercuric oxide. The experiments were many times repeated.

Experiment 3.—Numerous tests were made with weaker creatinin solutions containing amounts corresponding with those in urine. Here the volume of mercury solution used was always relatively a little greater, suggesting a combination of 1 molecule of creatinin with $2\frac{1}{2}$ molecules of mercuric oxide, but the difference is doubtless due mainly to the slight excess required to give a reaction in dilute solution.

Experiment 4.—In titrating mixtures of urea and creatinin the same general difference was found as last shown, the reaction with urea being apparently slightly retarded by the presence of the creatinin. Tests of mixtures were made in large number so that the result may be looked upon as well established.

The final value of all these reactions may then be expressed as follows, the corrections being those necessary for average normal urine:

6	mg.	NH_3	in	20	cc.	(10	cc.	urine,	10	cc.	water)	require	1.0	cc. Hg sol.
7.5	"	$C_5H_4N_4O_3$	"	20	"	10	"	"	10	"	"	"	0.15	" " "
14.0	"	$C_4H_7N_3O$	"	20	"	10	"	"	10	"	"	"	0.85	" " "
													2.00	

The average correction to be made then on the Liebig titration is 2 cc. of the mercuric solution, but as readily seen this can be applied to fresh urine only since in old urine the effect of the ammonia of decomposition becomes too great to be easily corrected. In the clinical examination of fresh urine the correction may be applied with only a small margin of error, while in fuller analyses, where the disturbing factors are also estimated, it may be used with considerable accuracy. My thanks are due to Mr. Grulee, who made many of the experiments above.

NORTHWESTERN UNIVERSITY, CHICAGO,
July 20, 1901.

ON THE DETERMINATION OF FORMALDEHYDE.

BY A. G. CRAIG.

Received July 10, 1901.

THE methods for the determination of formaldehyde may be classed, by their reactions, in three groups, as follows :

Group 1.—Depending on a specific reaction.

Group 2.—Formation of addition products with elimination of the elements of water.

Group 3.—Oxidation and reduction.

Group 1 contains :

(*a*) The ammonia method.[1]

$$6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O.$$

(*b*) The potassium cyanide method.[2]

$$KCN + CH_2O = N{\equiv}C{-}\overset{\overset{H_2}{\|}}{C}{-}O{-}O{-}K.$$

(*c*) The fixed alkali method.[3]

$$NaOH + 2CH_2O = NaOOCH + CH_2OH.$$

Group 2 contains :

(*a*) The hydroxylamine method.[4]

$$NH_2OH.HCl + CH_2O = CH_2NOH + HCl + H_2O.$$

(*b*) The aniline method.[5]

$$C_6H_5NH_2 + CH_2O = C_6H_5NCH_2 + H_2O.$$

The precipitate is weighed.

[1] L. Legler: *Ber. d. chem. Ges.*, **16**, 1333.
[2] G. Romijn: *Zischr. anal. Chem.*, **36**, 18.
[3] Legler: *Ber. d chem. Ges.*, **16**, 1333.
[4] Brochet and Cambier: *Compt. rend.*, **120**, 449.
[5] Trillat: *Bull. Soc. Chim.*, [3], **9**, 305.

(*c*) Same as above except that the excess is titrated.[1]

Group 3 contains most of the methods which have been proposed.

(*a*) The ammoniacal silver nitrate method[2] depends on the reduction of metallic silver when silver nitrate is boiled with ammonia and formaldehyde.

(*b*) The acid silver nitrate method.[3]

$$KClO_3 + AgNO_3 + 3CH_2O = 3CHOOH + AgCl + KNO_3.$$

(*c*) The iodine method.[4]

$$CH_2O + 2I + 2NaOH = 2NaI + CHOOH + H_2O.$$

(*d*) The alkaline permanganate method.[5]

(*e*) Another potassium permanganate method.[6]

(*f*) The bichromate method.[7]

(*g*) The hydrogen peroxide method.[8]

$$CH_2O + H_2O_2 + NaOH = NaOOCH + 2H_2O.$$

A careful study of the various methods and the comments on them brought out the fact that no fixed standard had been used to test the accuracy of the methods, but that the highest or the average results were taken to be the best.

A sample of trioxymethylene was prepared by evaporation. Trials were made of titration with potassium permanganate and oxalic acid. The end-point was sharp, and tests showed that the formaldehyde was completely destroyed.

The most successful scheme was as follows: 280 cc. bottles, having glass stoppers closed with graphite and tied down; trioxymethylene, about 0.5 gram.; 25 cc. 1 : 1 sulphuric acid; 40 cc. 1 per cent. potassium permanganate. The bottle is closed and heated to 80° C. for fifteen minutes. The solution is then cleared up with standard oxalic acid and titrated to pink. The results obtained were 96.4 per cent. and 96.0 per cent.

A trial was made of sealing some of the sample in a test-tube with water and heating. Solution was complete in one-half hour at 100° C. The results by titration were unsatisfactory. Fear-

[1] Klar: *Pharm. Ztg.*, **40**, 611.
[2] Orchard: *Analyst*, **22**, 4.
[3] Grützner: *Arch. Pharm.*, **234**, 634.
[4] G. Romijn: *Ztschr. anal. Chem.*, **36**, 18.
[5] Smith: *Analyst*, **21**, 148.
[6] Jones: *Am. Chem. J.*, **17**, 539.
[7] Nicloux: *Bull. Soc. Chim.*, [3], **17**, 839.
[8] Blank and Finkenbeiner: *Ber. d. chem. Ges.*, **31**, 2979.

ing that the sample might be impure, some of it was sublimed in a combustion tube tightly closed, with a cannon tube at one end and a condenser at the other. The pressure did not rise very high. The sublimate collected in and beyond the condenser, partly as a fine white powder, and partly as a solid mass. A brown tarry substance remained unvolatilized. A portion of the sublimate was sealed up with water and boiled. The boiling was continued every day for a week, but the sublimate did not dissolve.

An attempt was made to titrate the sublimate as above, but it required one hour at 95° to dissolve it, and results of 108.6 per cent. and 106.2 per cent. were obtained, showing that the permanganate was reduced by the heat.

The Grützner method was next tried: "Into a glass stoppered flask put 5 cc. of solution containing about 0.15 gram of formaldehyde, about 1 gram potassium chlorate, 50 cc. decinormal silver nitrate, and 1 cc. nitric acid. The closed flask is gradually warmed in the water-bath with frequent shaking. The reaction is complete in one-half hour. The end of the reaction is easily seen when the solution becomes clear above the silver chloride. The excess of silver nitrate may be titrated or the silver chloride may be weighed."

A sample of trioxymethylene was obtained from E. Merck, and portions were dried in the steam oven. Various experiments were made as to the best form of bottle, time, temperature, light, etc. By heating in blackened water to 80° C. and then one-half hour between 80° and 90°, filtering rapidly, and drying at 200° to constant weight, a pure white silver chloride was obtained, but the results in twenty determinations varied from 91 per cent. to 120 per cent. No reason could be found for this variation except in the inconstancy of the reaction. The Grützner method, then, seems to be altogether unreliable.

The Blank and Finkenbeiner method is as follows: "1 gram trioxymethylene or 2 cc. formaldehyde is placed in a flask and 25 cc. of double normal soda solution added. Then 50 cc. of hydrogen dioxide, of strength 2.5 per cent. or 3 per cent. is added cautiously, the addition lasting three minutes. Allow stand two to three minutes and titrate with sulphuric acid, using litmus."

The commercial hydrogen dioxide contained acid, which was either neutralized or titrated, usually the former. The trioxy-

methylene was found to dissolve easily in the solution on the addition of the hydrogen dioxide. It was found that it is necessary to allow the flask to stand ten minutes before titrating. Results were as follows:

	Per cent.
Allowed to stand ten minutes cold	92.2
Heated slowly ten minutes	91.9
Sample dried by heating in flask to 85° for fifteen minutes with slow stream of natural gas	95.8
Sample heated to 85° for one hour, then a slow stream of natural gas passed for ten minutes	96.9
Gas passed for seven hours cold	96.4
Heated one hour at 85°, gas passed fifteen minutes, and then allowed to stand over calcium chloride five days	97.5

These results showed that the trioxymethylene contained water, and that, in the limited time allowed, it was practically impossible to dry it. The substance is almost as volatile as water, especially when warmed, and long standing in desiccators seemed the only way of drying it thoroughly. It was impossible to tell when the substance was dry, as when it apparently contained as much as 8 per cent. of water it was powdery, not sticking to glass, nor showing the slightest dampness. This explains the variable results of the earlier experiments and will prove of value in interpreting the results.

The Legler method is as follows: "To a sample of formaldehyde in a flask a sufficient excess of normal ammonia is added, allowed to stand tightly corked, and titrated back, using litmus, to which hexamethylene tetramine is neutral."

According to G. Lösekann,[1] the amine is monobasic to methyl orange, and must be titrated to a full red. It was decided to use methyl orange in order to avoid error from the presence of carbon dioxide.

W. Eschweiler[2] states that accurate results can be obtained only by allowing to stand five days or by boiling for one hour. Carl E. Smith[3] states that it is necessary to allow to stand only fifteen minutes.

G. L. Taylor[4] directs to allow to stand twelve hours, and L. F. Kebler[5] says: "It is undesirable to report results on a reaction

[1] *Ber. d. chem. Ges.*, **22**, 1565.
[2] *Ibid.*, **22**, 1929.
[3] *Am. J. Pharm.*, Feb., 1898.
[4] *Ibid.*, April, 1898.
[5] *Ibid.*, Sept., 1898.

of less than six hours' duration. * * * Neither were the results constant for duplicate of the same sample. * * * In my opinion, the only reason that Professor Smith arrived at the results he did was because the number of samples worked on was too limited."

It was decided to boil one hour. Trials on the same sample showed that practically the same result was obtained by allowing to stand eighteen hours at 16°, and one hour at 100°,—93.1 per cent. for the former and 93.5 per cent. for the latter. The work was done with prescription bottles holding from 2 to 4 ounces, with soft rubber stoppers. Several attempts were made to dry the trioxymethylene, but as no 100 per cent. results could be obtained it was concluded that it was impossible to dry it in the limited time allowed for the first series of experiments.

A sample of commercial formaldehyde was tested, boiling in 2-ounce bottles for one hour, and titrating to full redness with methyl orange. The results were 37.34 per cent., 37.44 per cent. and 37.35 per cent. The Blank and Finkenbeiner method gives for this sample 37.30 per cent. These two methods are therefore in practical accord.

The chief difficulty in using the Legler method is the volatility of the normal ammonia. Carl E. Smith[1] proposes a way of getting rid of the standard ammonia by liberating ammonia from ammonium chloride by means of normal soda. In these experiments, the principal difficulty from the ammonia has been, not the loss of strength in the standard solution but the loss during the determination. This is not remedied by Professor Smith's modification.

By the following scheme both these sources of error are removed: Prepare a normal solution of sulphuric acid. Make up an approximately normal solution of ammonia, the exact strength being immaterial. Procure several 3-ounce prescription bottles with smooth sides and close-fitting soft rubber stoppers. Prepare a methyl orange solution. Procure a boiler in which the bottles may be immersed to the neck without upsetting (a large beaker will do). Take as much of the sample as will contain 0.5 gram of formaldehyde. Measure with the pipette, 25 cc. of the ammonia solution into each of the bottles, and to half of them add a sample of formaldehyde; stopper tightly. If the necks of the bottles are

[1] *Am. J. Pharm.*, Feb., 1898.

small, the stoppers need not be tied down. Place the bottles in the boiler, add cold water to the necks, and heat to boiling. Boil for one hour, and cool by running in cold water slowly, being careful not to allow the cold water to touch the hot bottles. Titrate with sulphuric acid and methyl orange, *to the first indication of a color change.* Take the difference between the readings for the blanks and those for the samples, as the ammonia consumed, in normal cubic centimeters. Of this difference, 1 cc. equals 0.0601 gram of formaldehyde.

Trials were made on the sample of trioxymethylene which was previously used, but which had been standing for one year. Results were obtained as follows: 99.8, 98.5, 100.0, and 100.1 per cent. On a sample of commercial formaldehyde, these results were obtained: 38.0, 37.7, 37.6, 37.8, 37.8, 38.1 per cent. As this work was done at night, probably better results could be obtained under better conditions.

These experiments indicate that Lösekann obtained good results by titrating to a full red, because the loss during the titration about equals the amount of acid added between the first color change and the full red; that is, about 0.25 cc. By following Lösekann's directions, fairly good results may be obtained with normal ammonia solution, without the use of a blank. The rubber stopper changes its shape during the heating, and probably a glass-stopper would be better if convenient, and if a secure fit could be made. From the results of these experiments it is observed that the reaction of the Legler method is quantitative, and that the results are as accurate as the means will allow. The same may be said of the Blank and Finkenbeiner method.

The Legler method has the advantage that it is cheaper, more convenient, and less subject to error from impurities than the sample. In using the Legler method, the maximum results can be obtained by boiling for one hour.

It must be remembered that the errors in the Legler method do not balance each other. The tendency is toward low results. Therefore, in any series of results, the higher results are likely to be the better. A blank determination is necessary. In the titration a correct end-point is very important. In both the Legler and the Blank and Finkenbeiner methods, any acid present must be accounted for.

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THE INDIRECT WEIGHING OF QUANTITATIVE PRECIPITATES. A RAPID AND ACCURATE METHOD FOR DETERMINING THE WEIGHT OF A PRECIPITATE WITHOUT SEPARATING IT FROM THE LIQUID FROM WHICH IT WAS PRECIPITATED.

By R. W. Thatcher.

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THANKS to the precision of the modern analytical balance, a gravimetric analysis, which consists essentially in the conversion of a weighed quantity of the substance to be assayed into an insoluble form, freeing it from impurities by washing, and drying and weighing it in the new form, is a process which is exact almost to the limit of perfection. But the difficulties in the way of properly preparing the material in a pure condition for subsequent weighing are many. The tendency of many precipitates to dissolve in the liquid used for washing out impurities, the mechanical adhesion of these impurities to the precipitated substance, and finally the difficulty of separation of the precipitate from the filtering medium, are too familiar to every analyst to need emphasis here. Many devices have been resorted to in order to obviate the errors arising from these causes, with the general result that an accurate gravimetric analysis is a process which requires considerable time for its completion and great care in its manipulation.

The disadvantages just alluded to have resulted in a very general attempt to devise volumetric methods which can be carried out with more ease and rapidity. Generally speaking, however, these volumetric methods, which are based upon the measurement of volumes of liquids which are known to contain definite proportions of the materials to be used, are open to serious criticism because of their inherent sources of error. Inaccuracies in calibration of the measuring apparatus, fluctuations in volume of solution due to changes in temperature, and changes in the composition of the dissolved material, give rise to serious errors, which are difficult to prevent and which greatly impair the value of this method of analysis.

It is obvious, therefore, that neither of these two classes of methods can be said to possess both of the requirements of an

ideal method of analysis, *viz.*, accuracy and rapidity. The desirability of some simple method by means of which the weight of a precipitated substance could be accurately determined without the necessity of first completely separating it from the liquid from which it was precipitated is apparent. Such a method would have the accuracy of a gravimetric process, without its attendant objectionable features, and would be more accurate than many of the volumetric methods. So far as I have been able to learn, no such method has been suggested up to the present time. That the operation is possible, however, is shown by the discussion below. That it is not only possible, but practicable and capable of wide application, is shown by the analytical data presented in a subsequent portion of this paper.

THE THEORETICAL DISCUSSION OF THE PROPOSED METHOD.

The formulas which are given below are based on facts which are so well known as to seem axiomatic; namely, that the weight of any substance is equal to its specific gravity times its volume; and conversely, that the volume of any substance is equal to its weight divided by its specific gravity.

If now a certain definite volume (which may be represented by b) of a mixture of a liquid and a solid, or precipitate, be weighed, the weight thus obtained is obviously equal to the sum of the weights of the liquid and the precipitate. Or, if the weight found be represented by a and that of the precipitate and liquid by x and y respectively, then

$$a = x + y. \qquad (1)$$

Now the weight of the liquid v is, as was stated above, equal to its volume times its specific gravity. Its volume is obviously the total volume of the mixture minus that of the precipitate, and the volume of the precipitate is its weight divided by its specific gravity. Or, if we represent the volume of the precipitate by v, and that of the liquid by v', and their specific gravities by d and d' respectively, then

$$y = v'd', \qquad (2)$$

$$v' = b - v, \qquad (3)$$

$$v = \frac{x}{d}. \qquad (4)$$

Combining 2, 3, and 4, we have

$$y = (b - \frac{x}{d})\, d'. \qquad (5)$$

Substituting this value for y in (1) the formula becomes

$$a = x + (b - \frac{x}{d})d', \qquad (6)$$

or

$$x = \frac{d(a - bd')}{d - d'}. \qquad (7)$$

In this formula a, the total weight, and b, the total volume, are known ; d, the specific gravity of the precipitate, is constant for precipitates of the same substance and can be determined once for all ; and d', the specific gravity of the liquid, can easily be determined. From these factors the value of x, the unknown weight of the precipitate, can be calculated.

From the above discussion it appears that in order to determine the weight of any precipitate without separating it from the liquid from which it was precipitated, it is only necessary to transfer the mixture to a vessel, the exact volume and weight of which is known ; weigh the whole; then draw off a portion of the liquid and determine its specific gravity. From this data and the known specific gravity of the precipitate, the weight of the latter can easily be calculated by means of the formula given above. This formula is a general one, and the process is, therefore, applicable to all precipitates of which the specific gravity is known or can be determined. The one condition by which its application is limited is, that the specific gravity of the precipitate must be constant, or, in other words, that the precipitate must always have the same composition. Most quantitative precipitates are of definite and invariable composition and hence meet this requirement. A few, however, vary in character with varying conditions of precipitation. This method of procedure could be used for determining the weights of such precipitates only when the conditions under which they were formed were so controlled as to insure uniformity in the composition of the precipitate.

Furthermore, the same formula, or modifications of it, will serve for other purposes. For example, if a known quantity of some substance is so treated as to produce a known weight of precipitate the specific gravity of the latter may be determined by a process identical with that described above. In this case x, the weight of the precipitate, will be known and d, its specific gravity, unknown. In order to simplify the calculation, the formula may be rearranged as follows :

$$d = \frac{d'x}{bd' + x - a}. \qquad (8)$$

Since no very satisfactory method for determining the specific gravity of solids in finely divided or amorphous condition has heretofore been proposed, the importance of this application of the formula is apparent. It is especially valuable in determining the specific gravity of those precipitates which decompose or change in composition during the washing and drying which is necessary in order to obtain them in a pure form.

Again, in case a substance can be readily obtained in pure condition, its specific gravity may be easily determined by placing a weighed quantity of it in the weighing-bottle and filling the latter with pure water, and weighing the whole. Since the specific gravity of the liquid in this case is known, no further data need be determined. The specific gravity of the solid can be computed from the formula (8), d' being a constant (*i. e.*, the specific gravity of water at the temperature at which the weighing is made), and bd' likewise a constant for the same weighing-bottle.

Further, since this method of determining specific gravity can be carried out very rapidly, it may serve as a means of determining the rate of change in composition of certain variable precipitates, as, for example, the rate of dehydration of the hydrated oxides of aluminum or iron. Some data bearing on this application of the formula was accidentally accumulated during the investigations upon the accuracy of this method of obtaining weights of precipitates, and will be published at some later time.

METHODS OF OPERATION.

Briefly stated, the principle upon which this new method for determining the weight of quantitative precipitates is based, is that if the weight of a definite volume of a mixture of two substances, whose specific gravities are known, be determined, the proportion of each which is present in the mixture may be calculated. An indirect determination of the weight of a precipitate without previously separating it from the liquid from which it was precipitated, based upon this principle, consists of the following processes: first, a determination of the weight of a measured volume of the precipitate and mother-liquor; second, the separation of a correct sample of the liquid from the precipitate; third, a determination of the specific gravity of this liquid; and fourth, a calculation of the weight of the precipitate by means of the

formula described above. A previous knowledge, or determination, of the specific gravity of the precipitate is, of course, necessary. The details of these operations and precautions to be observed in each are described below.

Specific Gravity of the Precipitate.—It should be noted that the same accuracy in the determination of the specific gravity of the precipitate as in that of the liquid is not necessary. In practical work with such mixtures, the relative amount of precipitate present will always be small and any inaccuracy in the determination of its specific gravity will produce a correspondingly small error.

None of the methods which have been proposed for the determination of the specific gravity of a solid substance are very well adapted to work with finely divided or amorphous precipitates. Determinations based upon the loss of weight of the material when immersed in a liquid require the preparation of the substance in a perfectly pure and dry condition, which in itself is as difficult as the preparation of such precipitates for quantitative analysis, and the use of specially constructed apparatus. Methods based upon a measurement of the volume, or displacing power, of a weighed quantity of the substance are exceedingly unsatisfactory when applied to substances in powdered form, because of their tendency when dry to enclose air. It was found that methods based upon the use of the new formula as arranged for specific gravity (8) afforded by far the most satisfactory method for this purpose. As has been pointed out, this formula may be applied in two ways: first, by using a known amount of the material with pure water as the liquid for completing the desired volume, and second, by producing a known amount of the desired material by precipitation, weighing the mixture, and afterward determining the specific gravity of the liquid.

In all the following work a Geissler specific gravity bottle, or pycnometer, with a thermometer ground in as a stopper and a capillary overflow tube provided with a glass stopper, was used as the vessel in which a definite volume of liquid, or mixture of solid and liquid, was weighed. Such a pycnometer having been selected and its weight and volume once accurately determined, it can be used for a long series of determinations without the necessity of recalibration, since changes in its weight or volume are very slight, or practically none at all. Two of these pycnometers

were used, one having a capacity of approximately 100 cc. and the other of about 50 cc. These were calibrated as follows: The pycnometer was carefully cleansed and dried and its weight accurately determined. It was then filled with distilled water, which had been recently boiled and then cooled to a temperature slightly below that at which the bottle was to be calibrated. The thermometer was inserted and the temperature of the water allowed to rise slowly, the pycnometer being frequently shaken to insure uniform temperature throughout the whole. When the thermometer indicated 20° (that being adopted as the temperature most convenient for the working conditions of this laboratory), the overflow tube was closed, the outside of the pycnometer carefully dried, and the whole immediately weighed. The pycnometer was emptied, refilled, and reweighed several times until an exact knowledge of its water content at 20° was obtained. This weight was then divided by 0.998213 (the specific gravity of water at this temperature), and the result taken as the volume of the pycnometer. The weighings were all corrected for a slight difference in the length of the balance arms but were not reduced to the weight *in vacuo*, as this was not deemed necessary for the purpose of ordinary analytical work. In order to determine the specific gravity of any insoluble substance of which a quantity of pure material was available, it was only necessary, then, to introduce a weighed quantity of it into a pycnometer which had been calibrated as described above; fill the latter with pure distilled water, properly cooled; bring the mixture to the temperature adopted in calibration; and complete the weighing as before. The specific gravity of the precipitate was then calculated from the formula. If the substance in question was in the form of a dry powder a little water was added to it after it had been weighed and the mixture stirred thoroughly to insure complete wetting of the material and exclusion of enclosed air bubbles. In case no supply of pure material of the substance whose specific gravity was to be determined was available, or could be prepared only with difficulty, the process was carried out exactly as will be described below for the indirect weighing of precipitates. In this case it was necessary to start with a known amount of some soluble material which was subsequently quantitatively precipitated in the desired form. The details of the method will appear in a subsequent paragraph.

Loevinsohn[1] has shown that the state of subdivision or mass of a substance has no effect upon its specific gravity, hence it is only necessary to insure that the composition of the precipitate shall be invariable in order that its specific gravity shall be constant, no matter what the conditions under which it was precipitated may be. The specific gravity of any invariable quantitative precipitate having been once accurately determined, this factor may be used for all subsequent indirect determinations of the weight of precipitates of this substance.

Weight of a Definite Volume of the Mixture.—Any apparatus, the exact volume of which is known, might serve as a weighing-bottle for the mixture, but since the volume and, conversely, the specific gravity of a liquid are affected by changes of temperature, a means of controlling or determining the latter is essential. A very small neck or opening which may be closed, in order to prevent evaporation of the liquid during weighing, is also very desirable for accurate work. The Geissler specific gravity bottle already mentioned is admirably suited to these needs.

The weighing-bottle having been prepared, the substance to be weighed was precipitated according to the method used in the ordinary analysis. After precipitation was complete, the mixture was cooled to a temperature slightly below that at which the pycnometer was calibrated. (The total volume of the mixture should not exceed two-thirds that of the pycnometer. If greater than this, the excess of liquid was removed by drawing it off through a filtering pipette.) A funnel with a short stem was placed in the neck of the pycnometer and the precipitate and mother-liquor were washed into it by means of a fine jet of cold water. After the precipitate was all washed in, the volume was completed with water which had been properly cooled, the water being allowed to flow down the sides of the pycnometer so as not to disturb the precipitate below and cause it to rise in the neck of the bottle. A very small amount of certain precipitates will rise to the surface by "creeping." In case this occurred, the material on the surface of the liquid was gently tapped with the bulb of the thermometer several times before inserting the latter. This generally sufficed to cause the floating particles to settle and thus prevent any loss of the precipitate. After the thermometer had been inserted, the capillary opening was closed with the

[1] Inaug. Diss., Berlin, 1883; abs. in *Ber. d. chem. Ges.*, **12**, 22.

finger, the bottle inverted, and its contents thoroughly mixed by shaking, so as to insure uniformity in the dilution of the liquid. This was repeated several times while the temperature of the liquid was rising to the desired point. When the thermometer indicated 20° the pycnometer was closed, dried, and immediately weighed. Except in very rare cases, no appreciable change in temperature occurred during the weighing, since the temperature of the balance case was usually but very slightly above that of the pycnometer. The weight thus obtained minus that of the pycnometer gave that of the volume of the mixture which the latter contained.

Separation of the Liquid from the Precipitate.—In order that the sample of liquid, which was withdrawn to be used in the determination of its specific gravity, should exactly represent the composition of the whole of the liquid, it was necessary that the process be rapid enough to prevent any concentration by evaporation, that the liquid should not be diluted by coming in contact with damp or wet apparatus, and that its separation from the precipitate should be complete. The ordinary method of filtration would generally result in a change in specific gravity through evaporation, and would be a return to one of the objectionable features of the usual methods of analysis. Two methods for accomplishing the desired result suggested themselves: first, the withdrawal of the desired sample by means of a filtering pipette, and second, a mechanical subsidence of the precipitate by means of a centrifugal and subsequent drawing off of a sample of the clear supernatant liquid. The use of a filtering pipette would afford a very convenient and rapid means of withdrawing a portion of clear liquid from the mixture, if the precipitate were in granular or crystalline form, but in the case of those precipitates which tend to clog up the filter or are so finely divided as to partially pass through the ordinary filtering media, the process is much less satisfactory. Moreover most of the forms of filtering pipette which have yet been suggested are more or less difficult to clean and dry rapidly.

Hence, in nearly every determination which was made in the present work the second method of separating the liquid from the precipitate was employed. The only centrifugal which was available was an old form of the Babcock milk tester. This was used with very satisfactory results. The separation was accomplished

as follows: The mixture in the pycnometer was shaken gently to insure uniform composition of the liquid and a portion of it poured into a large, clean, dry test-tube. The latter was placed in the centrifugal and whirled until the precipitate settled completely, leaving a clear, supernatant liquid. For most of the precipitates this required less than one minute. Barium sulphate and aluminum hydroxide required a little longer, but in no case was it necessary to spin the apparatus longer than three minutes. Evaporation of the liquid during this time was, of course, very slight and could be entirely prevented by closing the test-tube with a cork. As soon as the supernatant liquid was free from floating particles of the precipitate, a sufficient amount of it to fill the smaller pycnometer was drawn up into a dry pipette and its specific gravity determined. Duplicate samples drawn from various depths in the tube showed no appreciable variation in density.

Specific Gravity of the Liquid.—The determination of the specific gravity of the liquid component of the mixture is the most critical operation in the whole process. A single computation of the weight of a precipitate by means of the new formula will suffice to show that any very large error in the fifth decimal place of the factor for the specific gravity of the liquid will produce a small error in the fourth decimal place (or tenths of milligrams) of the weight obtained. It is therefore essential that the method to be adopted for determining the specific gravity of the liquid shall be capable of giving results with considerable accuracy to the fifth decimal place. This excludes the use of ordinary areometers, specific gravity balances, etc., and limits the operator to the use of specific gravity bottles of the best form. It has been shown by many analysts, however, that the Geissler pycnometer if carefully controlled will give results which are very accurate to the fifth decimal place. Extreme care, such as is used in the best of physical-chemical operations, will give results very closely approximating the truth in the sixth place, but such accuracy as this is not necessary for ordinary analytical work.

This method of determining the specific gravity of a liquid was therefore chosen as the one best adapted to the purposes of the present work. The process of such a determination is too familiar to all analysts to need detailed description. The pycnometer was filled with the liquid in question in exactly the same manner as it

was filled with water in calibration, and weighed under the same conditions. The weight of the liquid thus obtained, divided by the weight of the same volume of water, corrected for the specific gravity of water at the temperature of the weighing, gave the specific gravity of the liquid.

Calculation.—The calculation of the weight of the precipitate from the data obtained as described above was a comparatively simple process. The factor b in the formula, representing the volume of the large pycnometer, is a constant which in every calculation is to be multiplied by the specific gravity of the liquid. A table showing the product obtained by multiplying this factor by each of the digits, was prepared, which greatly facilitated the calculation.

Effect of Variations in Formula for Precipitate.—The exact composition of some of the common quantitative precipitates when in the moist condition is not known, since they may contain some chemically combined water which they lose on being dried for an analysis. Such a knowledge is not absolutely necessary for the purpose of this method of determining their weight, however. If a certain formula be assumed to represent the composition of such a precipitate and its specific gravity calculated on this basis, it is obvious that a weight calculated from the specific gravity thus obtained will be correct even though the formula which was adopted does not correctly represent the nature of the substance. The error in the determination of the specific gravity will be repeated in the opposite direction in the subsequent calculation and a correct result will thus be obtained.

It is, however, absolutely essential that the nature of the precipitate shall be the same under the conditions of the determination of its weight as under those which accompany the determination of its specific gravity. For those precipitates whose composition is likely to vary with the conditions under which they are produced, the determination of their specific gravity by the same process as is to be used later in weighing is the best method to pursue, since it will obviate any errors due to change in the nature of the precipitate. As has been shown, it is possible to do this by producing the precipitate in such a manner that its weight may be known, and its specific gravity calculated by the proper arrangement of the new formula.

EXPERIMENTAL WORK.

In order to test the accuracy of the new method of obtaining the weights of quantitative precipitates and also to compare this method with the older ones with regard to simplicity of manipulation, a large number of determinations of the weights of precipitates obtained from chemically pure material by the best methods of quantitative precipitation were made. In general those precipitates which are of considerable technical importance and which are subject to peculiar disadvantages when weighed by the usual gravimetric methods, were selected for this experimental work.

Estimation of Chlorine as Silver Chloride.—Rodwell[1] states that the specific gravity of silver chloride is 5.505 at 0° C. and 4.919 at the melting-point. Mohr[2] gives the figure 5.7 as the specific gravity of silver chloride but does not state the conditions under which the determination was made. Loevinsohn[3] gives the following as the average results of several determinations of the specific gravity of silver chloride in different physical forms: freshly precipitated, 5.5667; dried, 5.5667; melted, 5.5549. Schröder,[4] in his work on the molecular volume of silver chloride, obtained results for its specific gravity which varied from 5.517 to 5.594 with an average of 5.553.

These results vary so widely as to make it impossible to determine from them what the true value for the specific gravity of silver chloride is. It was therefore necessary to make a series of determinations, in order to obtain a correct factor to be used in the subsequent work of determining chlorine as silver chloride.

Since silver chloride decomposes quite rapidly when exposed to the light, several known quantities of pure silver chloride were produced immediately before beginning this work as follows: Measured portions of a standard hydrochloric acid solution (the exact chlorine content of which had been previously determined) were precipitated with silver nitrate according to the method usually adopted for that purpose. The precipitate in each case was transferred to a large test-tube and whirled in the centrifugal. In this way the precipitate was quickly collected in a compact mass at the bottom of the tube and the supernatant liquid could

[1] *Proc. Roy. Soc.*, **25**, 280.
[2] Pogg. *Ann.*, **113**, 655.
[3] Inaug. Diss., Berlin, 1883.
[4] *Ann. Chem.* (Liebig), **192**, 295.

be almost entirely drawn off by means of a filtering pipette without disturbing the precipitate. The latter was washed with hot distilled water in this way until the washings gave no test for silver. The pure silver chloride thus obtained was perfectly white, the process being of so short duration as to prevent any decomposition.

The precipitate was immediately washed into a pycnometer, the latter filled with pure distilled water and weighed under the conditions outlined in the previous description of the method for determining specific gravity of precipitates. The following are the results of the determinations.

TABLE I.—SPECIFIC GRAVITY OF SILVER CHLORIDE.

	Hydrochloric acid taken. cc.	Silver chloride equivalent. Gram.	Calculated specific gravity.
1	30	0.4573	5.5591
2	40	0.6098	5.5561
3	35	0.5335	5.5455
4	45	0.6860	5.5680
		Average,	5.5570

A sample of chemically pure sodium chloride was finely pulverized, dried in an air oven at 120° for an hour, and several samples of this powder weighed out for analysis. Each weighed sample was dissolved in distilled water, the solution heated to boiling, and the chlorine precipitated by silver nitrate solution, according to the usual method. The mixture was then cooled down to about 18°. It was then washed into the large pycnometer, brought to the proper temperature, and weighed. The precipitate settled so completely during the weighing that it was not necessary to whirl the mixture in the centrifugal in order to obtain a clear liquid for the specific gravity determination. After weighing, therefore, the mixture was cooled slightly, a portion of the clear supernatant liquid drawn off, transferred to the smaller pycnometer, weighed as soon as it reached the proper temperature, and the specific gravity calculated. From these data the weight of the silver chloride found was calculated. The following are the results which were obtained:

TABLE II.—DETERMINATIONS OF CHLORINE IN SODIUM CHLORIDE.

	Sodium chloride taken. Grams.	Silver chloride found. Grams.	Chlorine equivalent. Gram.	Chlorine found. Per cent.
1	0.8164	1.9998	0.4946	60.58
2	1.0205	2.5085	0.6202	60.76
3	1.0342	2.5320	0.6262	60.56
4	0.6186	1.5233	0.3757	60.73
5	0.4823	1.1851	0.2931	60.76
6	0.6877	1.6899	0.4179	60.75

The theoretical amount of chlorine in sodium chloride is 60.60 per cent. The results shown above are therefore within the limit of experimental error. They are no better than may be obtained by the ordinary methods of weighing, however. These determinations were the first that were made by the new process and it is probable that with more experience in manipulation better results would have been obtained. The process, however, does not offer any especial advantage over the usual gravimetric analysis in the case of a precipitate which is so easily prepared for weighing as is silver chloride. Should some substance which would render the washing of the precipitate tedious or difficult to complete be present in the solution, this new method might be of value.

Estimation of Sulphur as Barium Sulphate.—Several determinations of the specific gravity of barium sulphate by the older methods have been published. Mohr[1] gives 4.446 as the result obtained when the dried precipitate was used. Karsten[2] used ignited material and obtained 4.2003 as its specific gravity. Rose[3] made two determinations, using freshly precipitated salt with an average result of 4.5262. Schröder,[4] during his work on molecular volumes, made several determinations under different conditions and gives results varying from 4.022 to 4.512 with a mean value of 4.330. Wiedemann[5] made four determinations, using water at 14.9° as the standard of comparison. He obtained very concordant results, the average being 4.3962. None of these results being satisfactory for the present work, preliminary determinations of the specific gravity of barium sulphate were necessary. A quantity of pure barium sulphate was dried in the

[1] See Böttger's "Tabell. über dem Spez. Gew. Körpern."
[2] Schweigger's *Journal*, **63**, 394.
[3] Pogg. *Ann.*, **75**, 409.
[4] *Ibid.*, **106**, 226.
[5] *Ibid.*, [5], **15**, 371.

oven at 140° and varying amounts of this material were weighed out for the determination of specific gravity. Each weighed portion was washed into the pycnometer and the latter filled with distilled water and the determination of specific gravity completed as usual. The following results were obtained:

TABLE III.—SPECIFIC GRAVITY OF BARIUM SULPHATE.

	Barium sulphate taken. Grams.	Calculated specific gravity.
1	3.7251	4.2982
2	1.6317	4.3330
3	2.0868	4.3225
4	1.2738	4.3293
5	3.0931	4.3000
6	2.8593	4.2791
7	1.7795	4.3062
		Average, 4.3098

The factor 4.31 was assumed as representing the correct value for the specific gravity of barium sulphate and was used in all subsequent determinations of the weight of precipitates of the latter.

A quantity of chemically pure potassium sulphate was finely pulverized, dried in the air-oven, and cooled in a weighing-bottle. Six samples were weighed out from this bottle into separate beakers. Each sample was dissolved in distilled water, 10 cc. of concentrated hydrochloric acid added, the solution heated nearly to boiling, a slight excess of barium chloride solution added, and the mixture boiled for a few minutes. After standing for a short time a part of the clear supernatant liquid was drawn off so as to reduce the total volume to about half that of the large pycnometer. The remainder of the mixture was then cooled, washed into the pycnometer, and the latter filled and weighed as usual. After this weighing the liquid in the pycnometer was thoroughly mixed by shaking, then poured into a large test-tube, the latter placed into the centrifugal and whirled until the precipitate had completely subsided. This required two or three minutes and the temperature of the liquid was raised several degrees. As soon as the supernatant liquid became clear, a portion of it was drawn off, cooled, transferred to the smaller pycnometer and its specific gravity determined. From the data thus obtained the weight of the barium sulphate precipitate was calculated. The following are the results obtained:

TABLE IV.—DETERMINATIONS OF SULPHUR IN POTASSIUM SULPHATE.

	Potassium sulphate taken. Grams.	Barium sulphate found. Grams.	Sulphur equivalent. Gram.	Sulphur found. Per cent.
1	2.4887	3.3581	0.4612	18.53
2	2.8379	3.8583	0.5299	18.67
3	2.2032	2.9823	0.4096	18.58
4	0.9574	1.2759	0.1753	18.32
5	0.6000	0.8063	0.1107	18.45
6	0.6459	0.8664	0.1190	18.42

The theoretical amount of sulphur in potassium sulphate is 18.40 per cent.

The determinations recorded above are all that were made by the new method and may therefore be regarded as showing what may be expected of this method in ordinary work. They show that if the amount of barium sulphate precipitated is not too large, very satisfactory results are obtained. Even with the very large amounts of precipitate obtained in Nos. 1, 2, and 3 above, the results compare very favorably with those which it is possible to obtain by the ordinary methods of weighing this precipitate. The whole process of determining the weight of barium sulphate precipitate by this method requires less than thirty minutes' time. The very difficult and tedious process of washing the barium sulphate free from impurities is unnecessary and all danger of loss of precipitate, because of its slight solubility in the water used for washing it, is avoided. This method as applied to the determination of the weight of a precipitate of barium sulphate may therefore be carried out with very much more rapidity and is much less susceptible to error than any of the methods now in use.

Estimation of Calcium as Calcium Oxalate.—The only results of determinations of the specific gravity of calcium oxalate are those published by Schröder.[1] He gives the following values for the precipitate at 4° : 2.181, 2.182, and 2.200. Previous work along this line being so meager, it was necessary to make a sufficient number of determinations to insure a very reliable average result. No pure calcium oxalate being available, a few perfect crystals of Iceland spar were selected as the starting-point for this work. These were ground to a fine powder in an agate mortar. The powder was then dried thoroughly and three portions of it weighed out into separate beakers. These were each dissolved in dilute

[1] *Ber. d. chem. Ges.*, **12**, 561.

hydrochloric acid, the solution heated to boiling, ammonia and a slight excess of ammonium oxalate added, and the whole boiled gently for a few minutes. Souchay and Lenssen[1] have shown that under these conditions a stable precipitate having the composition $CaC_2O_4.H_2O$ is formed. These precipitates were washed by decantation, as described in the case of silver chloride, until free from chlorides, and their specific gravity determined by weighing with pure water. The results obtained are indicated by Nos. 1, 2, and 3 in the table below. From the same material a fourth portion of exactly 10 grams was weighed out, transferred to a liter flask, and dissolved in dilute hydrochloric acid. The volume was completed to the mark and four aliquot portions immediately drawn off before any appreciable change in volume due to rise in temperature had occurred. The calcium in these solutions was then precipitated as described above. The specific gravity of these precipitates was then determined by the usual method without separation from the mother-liquor. The results obtained are indicated by Nos. 4 to 7 inclusive in the table below.

TABLE V.—SPECIFIC GRAVITY OF CALCIUM OXALATE.

	Calcium carbonate taken. Grams.	Calcium oxalate equivalent. Grams.	Calculated specific gravity.
1	1.2594	1.8261	2.2524
2	1.5230	2.2083	2.2461
3	1.4184	2.0567	2.2418
4	1.0000	1.4500	2.2425
5	0.5000	0.7250	2.2528
6	1.0000	1.4500	2.2433
7	0.5000	0.7250	2.2470
		Average,	2.2465

Three aliquot portions of the solution of Iceland spar in hydrochloric acid described above were measured out, and two other samples of the finely ground material were weighed out and dissolved in dilute hydrochloric acid. The calcium was precipitated from the boiling solution by ammonia and ammonium oxalate and the precipitates allowed to stand until cool. The indirect weighing of these precipitates was then carried out as previously described, with the following results:

[1] *Ann. Chem. Pharm.*, **100**, 322.

TABLE VI.--DETERMINATIONS OF CALCIUM IN ICELAND SPAR.

	Calcium carbonate taken. Grams.	Calcium oxalate found. Grams.	Calcium equivalent. Gram.	Calcium found. Per cent.
1	1.0000	1.4483	0.4000	40.00
2	0.5000	0.7266	0.2007	40.14
3	0.5000	0.7251	0.2002	40.04
4	1.0009	1.4542	0.4019	40.15
5	1.0785	1.5595	0.4207	39.97

The theoretical amount of calcium in calcium carbonate is 40.04 per cent. The results obtained are therefore well within the limits of experimental error. The weighing of the precipitate by this method does not require more than thirty minutes' time, so that a complete gravimetric determination of calcium by this method may be made in less than one hour and the results are as accurate as can be obtained by the best of the present methods. The washing of the precipitate and its subsequent conversion into carbonate or oxide by ignition are therefore unnecessary.

Estimation of Phosphoric Acid as Ammonium Phosphomolybdate.—The estimation of phosphoric acid is one of the most important as well as one of the most difficult problems which the technical analyst has to solve. Its precipitation as ammonium phosphomolybdate is now almost universally adopted, because this compound serves to effect the separation of phosphoric acid from other bodies and possesses the added advantage of being a readily subsiding precipitate. Earlier experimenters have considered that the composition of the compound is somewhat variable[1] and that its conversion into some more stable form prior to the final weighing is therefore necessary. More recently Hundeshagen,[2] in his analytical studies of this compound, has shown that its composition under all conditions, when free from molybdic acid and other impurities, is $12MoO_3.PO_4.3NH_4$. It is quite difficult to obtain the precipitate free from impurities, however, and nearly all the gravimetric methods now in use require the solution of the precipitate in ammonia and its subsequent precipitation as magnesium ammonium orthophosphate, the latter being ignited and weighed as magnesium pyrophosphate, or titrated volumetrically. There are numerous difficulties in this process. Bergami[3] is of the opinion that magnesium oxide is frequently thrown out along

[1] Fresenius' "Quantitative Analysis," p. 199.
[2] *Chem. News*, **60**, 168, 177, 188, 201, 215.
[3] Bull. 43, Division of Chemistry, U. S. Dept. Agr., p. 99.

with the phosphate precipitate, which produces too high results. Furthermore Gooch and Austin[1] found that if too much ammonium salts are present in the solution the precipitate is apt to be partially converted into a metaphosphate on ignition, which will likewise yield too high results when calculated back to phosphoric acid. These difficulties have led to numerous attempts to execute the final determination directly upon the yellow precipitate. Carnot[2] has shown that, with proper precautions, the yellow salt may be reprecipitated from its ammoniacal solution, washed dried at 100°, and weighed. This method has not come into very general use, however, since great care must be exercised to prevent loss of the precipitate during washing. Pemberton[3] has suggested a volumetric method for titrating the yellow precipitate, which has been modified by Kilgore[4] so as to yield fairly satisfactory results. It is open to the general objections of all volumetric methods of analysis, however. Kilgore's results show that within certain limits a precipitate of constant composition, free from molybdic acid, may be obtained. The new method is, therefore, applicable to this precipitate. Its desirability is apparent, since it will avoid the danger of loss of the material, because of its slight solubility in the wash-water, and at the same time afford a simple gravimetric method for determining the weight of the precipitate.

No determinations of the specific gravity of this yellow precipitate have yet been published. It was therefore necessary to accurately determine this factor before attempting to test the applicability of the new method to the weighing of this precipitate. Two methods of procedure were adopted. For the first a quantity of the yellow precipitate, which had been accumulated in previous work, was carefully purified by repeated washing and portions of it suspended in pure water properly cooled and weighed in the pycnometer at 20° as usual. After weighing, the contents of the pycnometer were rinsed into a white dish, dissolved in a measured excess of carefully standardized potassium hydroxide solution, and the excess of the latter titrated back with standard nitric acid according to Kilgore's method. From the amount of potassium hydroxide required, the weight of the ammonium phosphomolybdate

[1] *Am. J. Sci.*, 1899, pp. 187–198.
[2] *Bull. Soc. Chim.*, Paris, 1893, 343.
[3] This Journal, **15**, 382; **16**, 278.
[4] Bull. 43, Division of Chemistry, U. S. Dept. Agr., p. 91.

present in the mixture was calculated. This weight and the weight of the mixture in the pycnometer afforded the data necessary for the calculation of the specific gravity of the precipitate. The results obtained are indicated by Nos. 1 to 4 inclusive in the table below. For the second series of determinations a quantity of pure disodium phosphate was obtained by recrystallization, and dried between filter-paper. A weighed portion of this was dissolved in water, and aliquot portions of this solution precipitated exactly as required by the Kilgore volumetric method, since this has been shown to give a precipitate free from molybdic acid. The specific gravity of these precipitates was determined by the usual method without separating them from the mother-liquor. Four determinations, using in each case 15 cc. of the solution which contained 0.01119 gram of disodium phosphate per cubic centimeter, were made, with the results indicated by Nos. 5 to 8 inclusive in the following table:

TABLE VII.—SPECIFIC GRAVITY OF AMMONIUM PHOSPHOMOLYBDATE.

	Ammonium phosphomolybdate equivalent. Grams.	Calculated specific gravity.
1	1.4600	4.011
2	1.4602	4.079
3	1.9405	4.050
4	2.9102	4.074
5	0.8793	4.040
6	0.8793	4.055
7	0.8793	4.086
8	0.8793	4.032
		Average, 4.055

For the purpose of testing the accuracy of the new method of weighing to the phosphoric acid precipitates, seven determinations of the percentage of phosphoric acid in pure disodium phosphate were made. Two further aliquot portions were drawn from the solution which was used in the specific gravity determination; a second solution was made up and three aliquot portions of this were taken. Finally two small samples of the material were weighed in two beakers and dissolved in water. The phosphoric acid in each solution was precipitated as in Kilgore's method, the mixture cooled, and the indirect weighing of the precipitate completed as usual. The following are the results of the analyses, stated in the same order as mentioned above.

TABLE VIII.—DETERMINATIONS OF PHOSPHORIC ACID IN DISODIUM PHOSPHATE.

	Disodium phosphate taken. Gram.	Ammonium phosphomolybdate found. Grams.	Phosphorus pentoxide equivalent. Gram.	Phosphorus pentoxide found. Per cent.
1	0.1679	0.8796	0.03330	19.83
2	0.1679	0.8747	0.03309	19.71
3	0.3144	1.6554	0.06253	19.89
4	0.2695	1.4111	0.05339	19.81
5	0.3593	1.8962	0.07164	19.94
6	0.2328	1.2238	0.04630	19.84
7	0.2486	1.2974	0.04909	19.74

The theoretical percentage is 19.82

All calculations were based upon the formula $12MoO_3.PO_4.3NH_4$ for the yellow precipitate. Carnot stated that the precipitate when dried at 100° contains water of crystallization as represented by the formula $24MoO_3.P_2O_5.3(NH_4)_2O.3H_2O$. Whether or not this be correct, no error is produced by the assumption of the more commonly accepted formula since the latter was used in calculations of the specific gravity also. These determinations show that if proper care in manipulation is exercised, this simple method is capable of yielding very accurate results with this precipitate which has heretofore caused analysts so much trouble. The only extra precaution which is required in this application of the method is that the precipitate must always be thrown down under similar conditions, since otherwise it is apt to be contaminated by impurities.

Specific Gravity of Cuprous Oxide.—F. W. Clarke in his "Tables of Specific Gravity"[1] cites the following results of determinations of the specific gravity of this precipitate: 6.052 and 6.093;[2] 5.751;[3] 5.750;[4] 5.746;[5] 5.300, 5.342, and 5.375.[6]

The limitations of our library have prevented my verification of these figures, or study of the conditions under which the determinations were made.

The cuprous oxide which is precipitated from boiling Fehling's solution by reducing sugars is supposed to be more or less hydrated. The degree of this hydration probably varies with the concentration of the solution, etc. Moreover, cuprous oxide is

[1] Bull. of the U. S. Geological Survey, 1886.
[2] Herapath: *Phil. Mag.*, **64**, 321.
[3] Karsten: Schweigger's *Journal*, **65**, 394.
[4] Leroyer and Dumas: Böttger's "Tab. Unters. d. Spez. Gew."
[5] Playfair and Joule: *Mem. Chem. Soc.*, **3**, 82.
[6] Peroz: *J. prakt. Chem.*, **47**, 84.

quite easily oxidized to the cupric condition. These facts make the preparation of a known quantity of pure cuprous oxide a somewhat difficult task. It is probable, however, that within the extremely narrow limits to the conditions of carrying out the reduction as prescribed by the methods now adopted by the Official Agricultural Chemists, the composition of the precipitate is practically invariable. The amount of precipitate produced varies with the time during which the sugar solution is boiled with the Fehling solution. Since it is almost impossible to keep this time always exactly the same, the use of a known amount of a reducing sugar in order to obtain a known amount of cuprous oxide is not sufficiently accurate for the purposes of this work. It was determined therefore to precipitate several quantities of the cuprous oxide according to the official method, wash them thoroughly, use the pure material thus obtained for the specific gravity determination, and afterwards dissolve the precipitate and determine the copper therein by some standard method. Five such precipitates were prepared and their specific gravity determined, the amount of copper present in each case being determined by titration with standard potassium cyanide solution. The following results were obtained:

TABLE IX.—SPECIFIC GRAVITY OF CUPROUS OXIDE.

	Potassium cyanide solution used. cc.	Cuprous oxide equivalent. Gram.	Calculated specific gravity.
1	85.6	0.5040	5.7000
2	76.3	0.4532	5.7336
3	81.7	0.4853	5.6788
4	77.3	0.4591	5.7058
5	84.6	0.4476	5.6852
		Average,	5.7007

The factor 5.7 was therefore assumed as representing very nearly the specific gravity of the cuprous oxide as precipitated under the conditions required by Allihn's method.[1] Since it is not necessary that the exact nature of the precipitate be known, or that the formula assumed to represent its composition be exactly correct, it was not deemed essential that any allowance for hydration of the precipitate be made. In all this work, therefore, the precipitate was considered as being simply cuprous oxide, and all calculations were made on this basis.

[1] Bull. 46, rev. ed., Division of Chemistry, U. S. Dept. of Agr., p. 35.

Determinations of Invert Sugar.—For the purpose of testing the accuracy of this method as applied to the weighing of cuprous oxide precipitated by invert sugar, a standard solution of the latter was made up, as follows: A quantity of pure sucrose (rock-candy) was pulverized and dried in the oven. 2.5 grams of this material were dissolved in 50 cc. of water and inverted according to the method of Clerget.[1] The solution was cooled, the excess of acid carefully neutralized with dilute sodium hydroxide solution, and the volume made up to 250 cc. One cc. of this solution contained, therefore, the equivalent of 0.01 gram sucrose or 0.010526 gram invert sugar. Several portions of this solution were measured out from a burette and boiled with Fehling's solution as prescribed by Allihn's method. It was found that if the mixture were allowed to stand in cold water until cool enough to weigh as usual, too high results were obtained because of a gradual deposition of cuprous oxide during the cooling. It was therefore decided to separate the precipitate from the mother-liquor as quickly as possible. After boiling for the prescribed two minutes, the mixture was poured into large test-tubes and the latter whirled in the centrifugal. The precipitate settled so quickly and so completely that the mother-liquor could be drawn off within thirty seconds from the completion of the boiling. The precipitates were then washed in the test-tubes with hot water, as described for the purification of the silver chloride precipitate. Two washings were always sufficient to leave no trace of alkali in the wash-water. The pure precipitate was then washed into the pycnometer with pure water, properly cooled, and the weight ascertained as usual. The following results were obtained:

TABLE X.—DETERMINATIONS OF INVERT SUGAR.

	Invert sugar taken. Gram.	Cuprous oxide found. Gram.	Invert sugar equivalent. Gram.	Error in milligrams.
1	0.2150	0.4026	0.2148	—0.2
2	0.1889	0.3935	0.1891	+0.2
3	0.2311	0.4311	0.2311	..
4	0.1896	0.3581	0.1890	—0.6
5	0.1595	0.3048	0.1592	—0.3

Since in this case the liquid portion of the mixture is water at a constant temperature, the only variable in the formula for calculation is a, the weight of the mixture. Hence the calculation can

[1] Bull. 46, rev. ed., Division of Chemistry, U. S. Dept. Agr., p. 39.

be much simplified by rearrangement of the formula, so as to combine all the constants of the operation into a single factor as follows:

Let c represent the weight of the pycnometer and contents.

Let c' represent the weight of the pycnometer.

Then

$$a = c - c'$$

and the formula

$$x = \frac{d(a - bd')}{d - d'}$$

becomes

$$x = \frac{d}{d - d'}(c - c' - bd') \text{ or } \frac{d}{d - d'}(c - (c' + bd')).$$

Now since Allihn's table for the dextrose equivalent of the precipitate is expressed in terms of copper instead of cuprous oxide, these results of the weighing must be divided by 1.1258, the factor for conversion of cuprous oxide into its copper equivalent. This is, of course, another constant in the calculation and may be introduced in the formula, which would then become

$$x(\text{in terms of copper}) = \frac{d}{(d - d')1.1258}(c - (c' + bd')).$$

Now the only variable in this formula is c, the weight of the pycnometer and contents. The whole expression may then be simplified as shown in the following example: In the determinations made above, the pycnometer weighed 41.7454 grams; its volume was 99.456 cc. The specific gravity of the precipitate was taken as 5.7 and of water at 20° as 0.998213. The quantity $(c' - bd')$ then became $(41.7454 + 99.456 \times 0.998213) = 141.0237$. The fraction

$$\frac{d}{(d - d')1.1258}$$

became

$$\frac{5.7}{(5.7 - 0.998213)1.1258} = 1.077.$$

The calculated amount of copper in any particular case was $(c - 141.0237)1.077$. For any other pycnometer, the value of c' and b would be different, but, once determined, they are constant and the corresponding factor may be easily calculated.

The whole process is, hence, extremely simple and may be carried out with great rapidity. After sufficient practice to

become familiar with the details of the work, a determination was easily completed in twenty minutes. While it is probable that the results are not quite so accurate as those obtained by the electrolytic estimation of the copper, they are as good as are usually required of a satisfactory method, and are subject to less variations than may easily be produced by slight changes in the conditions under which the reduction of the Fehling solution is carried out, which would affect the amount of cuprous oxide precipitated by a definite amount of reducing sugar. The method is capable of yielding more accurate results than may be obtained by the common volumetric methods for the estimation of copper, as is shown below. It possesses the added advantage that the mother-liquor is very quickly separated from the precipitate, thus diminishing the probability of the deposition of additional copper, as may happen in the case of the slower process of filtration by the other methods.

Determinations of Reducing Sugars in Commercial Glucose.—For the purpose of comparing the results obtained by this method with those obtained by the volumetric estimation of the copper, the following process was adopted. 2.25 grams of commercial glucose were dissolved in water and the volume made up to 250 cc. Aliquot portions of this solution were measured from a burette and the cuprous oxide precipitated as required by Allihn's method. The weight of cuprous oxide obtained was determined by the new method as described above; the contents of the pycnometer were then dissolved in dilute nitric acid, and the copper estimated by titration with standard potassium cyanide solution. The following results were obtained:

TABLE XI.—COMPARISON OF RESULTS OF NEW METHOD WITH CYANIDE METHOD.

	By new method.			By potassium cyanide titration.		
Solution taken. cc.	Cu_2O found. Gram.	Dextrose equivalent. Gram.	Dextrose per cc. Gram.	Cu_2O found. Gram.	Dextrose equivalent. Gram.	Dextrose per cc. Gram.
25.0	0.4078	0.2175	0.00870	0.4078	0.2175	0.00870
27.5	0.4476	0.2407	0.00875	0.4389	0.2357	0.00857
22.5	0.3723	0.1969	0.00875	0.3693	0.1953	0.00868
25.0	0.4089	0.2181	0.00872	0.4120	0.2199	0.00879

The potassium cyanide titration of copper has been in use in this laboratory for several years. The end reaction is somewhat difficult to detect, but with some experience in its use and proper

care in manipulation it has been found to give the most satisfactory results of any of the volumetric methods which have yet been tried. The determinations recorded above show that more concordant results may be obtained by the new method of weighing the precipitate than by the cyanide method of volumetric estimation.

Determination of Aluminum as Aluminum Hydroxide.—An attempt to apply this method of weighing to the aluminum hydroxide precipitate was made. The preliminary determinations of the specific gravity of the precipitate showed that the composition of the latter is not constant but varies with the time which elapses between the precipitation and the subsequent weighing of the precipitate. Considerable data bearing upon the rate of this change in composition has been accumulated and will be published at some later time. The work has proceeded far enough to show that it is probable that this method may be applied to the weighing of the aluminum hydroxide precipitate if proper conditions as to time, temperature, etc., are observed. Just what the most favorable conditions are, however, is not yet definitely determined.

CONCLUSIONS.

The work of investigating the applicability of this new method to the practices of technical analysis, is by no means complete. In fact, it is but just begun. Yet the results already obtained, which are embodied in this paper, seem sufficient to justify the belief that its application to the processes of gravimetric analysis will be a decided advance toward the much desired simplicity and ease of manipulation. They show that the use of this process greatly reduces the time required for a determination and at the same time yields very satisfactory results. A comparison of this method with the older ones when applied to the analysis of impure or mixed materials is yet to be made, but since many of the precipitates already experimented upon were weighed in the presence of solutions containing several other compounds, it is thought that the working conditions of these determinations very closely approximate those of ordinary analyses. The results already obtained, therefore, lead to the conclusion that the proposed method is a step toward the realization of the conditions of an ideal method of analysis, namely, accuracy and rapidity.

UNIVERSITY OF NEBRASKA, LINCOLN, NEBRASKA,
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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY NO. 60.]

THE ELECTROLYTIC DETERMINATION OF MOLYBDENUM.

BY LILY GAVIT KOLLOCK AND EDGAR F. SMITH.

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MORE than twenty years ago Smith,[1] in describing his experience in the electrolysis of solutions of ammonium molybdate, wrote: "The deposition, although complete, was so very slow that this method of determination was practically of little value." During the last few months attention has again been given in this laboratory to the subject. Sodium molybdate ($Na_2MoO_4.2H_2O$) was dissolved so that 0.1302 gram of molybdenum trioxide was present in 125 cc. of solution, which was exposed for several hours to the action of a current of 0.1 ampere and 4 volts. The temperature of the electrolyte was 75° C. No precipitation occurred upon either electrode. Upon adding two drops of concentrated sulphuric acid to the liquid, it at once assumed a dark blue color. As the current continued to act, this color disappeared and the cathode was coated with a black deposit—the hydrated sesquioxide.[2] On removing the colorless liquid and testing it with ammonium thiocyanide, zinc, and hydrochloric acid, evidences of the presence of molybdenum failed to appear. In the following experiments the molybdenum deposit was a brilliant black in color and so adherent that it could be washed without detaching any particles. Usually the colorless liquid was removed with a siphon, cold water being introduced without interrupting the current. The deposit was not dried, but while yet moist it was dissolved from off the dish in dilute nitric acid and the solution carefully evaporated to dryness, the residue being heated upon an iron plate to expel the final traces of acid. White molybdic acid remained. It was noticed several times that blue spots existed here and there in the mass, but these were removed by moistening the residue with nitric acid and evaporating a second time to dryness. This procedure was adopted in all the trials given below. Concordant results could not be obtained by merely drying the hydrate at a definite temperature. The same was true also on attempting to ignite the hydrate to trioxide. Loss then occurred from sublimation and volatilization.

[1] *Am. Chem. J.*, 1, 337.

[2] *Ibid.*, 1, 338.

RESULTS.

	Molybdenum trioxide present in grams.	Sulphuric acid added. cc.	Dilution. cc.	Temperature. °C.	Current.	Voltage.	Time. Hours.	Molybdenum trioxide found in grams.	Error in grams.
1	0.1302	0.1	125	70	$N.D._{.107} = 0.022$ A	2.0	$4\frac{3}{10}$	0.1299	— 0.0003
2	0.1302	0.1	125	80	$N.D._{.107} = 0.045$ A	2.25	$2\frac{1}{2}$	0.1302	....
3	0.1302	0.1	125	70	$N.D._{.107} = 0.04$ A	2.2	$4\frac{1}{2}$	0.1302	....
4	0.2604	0.2	125	75	$N.D._{.107} = 0.04$ A	2.0	7	0.2603	— 0.0001
5	0.1541	0.2	125	85	$N.D._{.107} = 0.04$ A	1.9	$2\frac{3}{8}$	0.1541	....
6	0.1541	0.2	125	80	$N.D._{.107} = 0.035$ A	2.1	4	0.1540	— 0.0001

The method is accurate, is easy of execution, and, as will be observed, requires comparatively little time. There seems to be no apparent reason why it should not replace some of the older and less reliable methods pursued in the determination of this element.

One of the first directions in which it seemed that the method could be made useful, was in the determination of the molybdenum content of the mineral molybdenite. By fusing the latter with a mixture of pure alkaline carbonate and nitrate, sodium molybdate and sulphate would be formed. If the sulphur was not to be determined, after dissolving out the fusion with water, and filtering out the insoluble oxides, it would only be necessary to acidulate the alkaline liquid with dilute sulphuric acid and proceed with the electrolysis; but in cases where an estimation of the sulphur was desired, it was thought that acetic acid would answer for the purpose of acidulation. To ascertain the latter fact the experiments given below were instituted. The solution, acidified with this acid, did not acquire a blue color on passing the current through it. The deposit of hydrated oxide was very adherent and was readily washed. It will, however, be noticed that a longer time is necessary for the complete precipitation. It is also advisable not to add the entire volume of acetic acid at first, but to introduce it gradually from time to time, from a burette.

RESULTS.

	Molybdenum trioxide present in grams.	29 per cent. acetic acid added. cc.	Dilution. cc.	Temperature. °C.	Current.	Voltage.	Time. Hours.	Molybdenum trioxide found in grams.	Error in grams.
1	0.1541	1	125	85	$N.D._{.107} = 0.075$ A	4.4	$7\frac{1}{2}$	0.1541	....
2	0.1541	1	125	85	$N.D._{.107} = 0.075$ A	4.4	3	0.1540	— 0.0001
3	0.1541	1	125	80	$N.D._{.107} = 0.05$ A	2.5	6	0.1543	+ 0.0002

In the last experiment, 5 grams of sodium acetate were added in order to increase the conductivity of the solution and also to ascertain what effect an excess of this salt would have, because, if the acetic acid were used to acidify the alkaline solution obtained by the decomposition of molybdenite, a great deal of this salt would be present. The concordant results justified the next step, which was to decompose weighed amounts of pulverized molybdenite with sodium carbonate and nitrate, then take up the fusion with water, filter out the insoluble oxides, acidify with acetic acid, boil off the carbon dioxide, and electrolyze. The liquid poured off from the deposit of the sesquihydroxide was heated to boiling and precipitated with a hot solution of barium chloride.

RESULTS OBTAINED FROM MOLYBDENITE.

	Molybdenite in grams.	Molybdenum found in per cent.	Sulphur found in per cent.
1	0.2869	57.37	38.28
2	0.1005	57.15	38.33
3	0.1388	56.83	37.87

MOLYBDENUM-SULPHUR RATIO.

(1)	1 : 2.004
(2)	1 : 2.012
(3)	1 : 1.998

From several experiments, which will not be recorded here, there is a possibility of separating molybdenum electrolytically from tungsten, the latter, of course, being present as an alkaline tungstate. Further work, however, will be necessary to fully establish this hope.

The experience detailed above proves conclusively that molybdenum must also be included in the list of metals which can be determined with the aid of the current and the analysis of molybdenite, as outlined, is vastly better than the usual procedures.

UNIVERSITY OF PENNSYLVANIA.

A COMPARISON OF THE SOLUBILITY OF ACETYLENE AND ETHYLENE.

BY SAMUEL AUCHMUTY TUCKER AND HERBERT R. MOODY.

Received June 12, 1901.

NO satisfactory or convenient method for the separation of acetylene and ethylene has yet been devised. The two gases exhibit such a similarity in their solubility that very few

reagents are known which will make a quantitative separation. The necessity for this separation arose while the authors were preparing ethylene which was generated simultaneously with acetylene from certain products produced in the electric furnace.

The reagents known to be good solvents for acetylene are water, ammoniacal or acid cuprous chloride, ammoniacal silver chloride or the nitrate, acetone, and alcohol; and those commonly mentioned as dissolving ethylene are bromine and sulphuric acid.

Wherever any mention is made of a separation of acetylene and ethylene it is generally taken for granted that the latter gas is completely insoluble in ammoniacal cuprous chloride, and the analysis is based upon this false assumption, Hempel being the one authority who takes a different view. The method suggested by him for the determination of acetylene although accurate was found undesirable owing to the length of time it takes for the analysis. This method is not recommended by the author for the separation of the two gases but merely as a means of determining acetylene. However, owing to the fact (stated later) that ethylene dissolves in cuprous chloride to form a soluble compound, this method is applicable to the separation of the two gases.

The method as used by us was carried out as follows: The cuprous chloride was contained in a train of five 5-inch U-tubes containing about 20 cc. each of the absorbent. To prevent the mechanical lifting of the precipitate into the connecting tubes, it was found desirable to use U-tubes with bulbs blown on each limb.

The mixed gases were collected over mercury in a pair of ordinary Hempel burettes, and from these delivered very slowly through the train of tubes. After all the gas was delivered from the burette, a T opening into the delivery tube was used for the introduction of nitrogen or hydrogen gas which acted as a sweep.

The red precipitate which was found in the tubes corresponds to $(Cu_2C_2H)_2O$. This was removed from the tubes, collected on a filter, washed to remove soluble copper compounds, dissolved in hydrochloric acid, converted to sulphate, and the copper deposited electrolytically. The quantity of acetylene in the original gas is easily calculated from this weight of copper. This method was tried repeatedly with good results, the only source of error being the possibility of loss through too rapid passage of the gas, and the only objection the amount of time consumed. In fact it is out of the question to make a rapid separation of the gases by

this method. Consequently an attempt was made to find a reagent which would absorb the acetylene and leave the ethylene undissolved.

The solvent action on ethylene of known absorbents of acetylene was first determined. The usual solvent recommended for acetylene is ammoniacal cuprous chloride. This solution is made up of 42 grams cupric chloride, 32 grams copper turnings, 100 cc. hot water, and 200 cc. commercial hydrochloric acid. The mixture is boiled for two or three hours and then a little concentrated hydrochloric acid added, and the whole boiled until it is pale yellow. This was cooled and an excess of ammonium hydroxide added. Such a solution was found to absorb acetylene rapidly and completely according to the following reaction :[1]

$$2Cu_2Cl_2 + 2C_2H_2 + H_2O = (Cu_2C_2H)_2O + 4HCl.$$

The next step was to investigate the solubility of known ethylene, this gas being generated by the action of metallic zinc on ethylene dibromide. Ethylene is so little soluble in water that there was no trouble to apprehend from such a small amount being absorbed. This was found by actual trial, and also the solubility in ammonium hydroxide. Here again a very slight solubility was noticed. Considering these two facts and that ethylene is not usually considered to be soluble in cuprous chloride, it seemed surprising, when either ammoniacal or acid cuprous chloride was added to a sample of ethylene to find that fully 95 per cent. of the gas was absorbed.

The foregoing is apparently not taken into account by Moissan whose results, according to the method of procedure given on pages 313 and 320 of "Le Four Électrique," can hardly be right. To be sure, the method is only spoken of in a vague way, but as stated in the reference given, it is natural to suppose that ethylene was considered as insoluble in the copper salt. If this were the fact, a large portion of the ethylene evolved from his thorium carbide must have been absorbed with the acetylene and counted with the latter.

Thinking that a mixture of ethylene and acetylene might act differently from either taken alone, equal volumes of the two gases were mixed and nearly the total volume was found to be absorbed by the copper solution. Other good solvents for acetylene are alcohol (1 volume of alcohol dissolves 6 volumes acety-

[1] Hempel's "Gas Analysis," p. 183.

lene) and acetone (1 volume of acetone dissolves 25 volumes acetylene). To investigate the possibilities of using either of these to absorb the acetylene and leave the ethylene the solubility of the latter gas was tried. Thirty cc. of pure ethylene were found to be all absorbed by acetone. Similarly when 100 cc. of ethylene were treated with an excess of 95 per cent. ethyl alcohol, a residue of less than 10 cc. was left, showing that both reagents were worthless for the purpose.

Since Nordhausen acid is such a good absorbent for ethylene, it seemed possible that it might first remove the ethylene and leave the acetylene. To determine this 56 cc. of known pure acetylene were passed several times into a Hempel pipette filled with the acid, and after two passages, over 60 per cent. of the acetylene was absorbed, showing that the reagent also failed in the required purpose. Finally the action of ammoniacal silver was investigated with the following results: The solution was made up by dissolving 10 grams silver nitrate in 500 cc. of water, making the solution barely acid with hydrochloric acid and then slightly ammoniacal. The clear solution thus obtained proved to be an excellent solvent for acetylene although it is slower in its action than ammoniacal cuprous chloride. The compound formed by its action is, according to Lewes,[1] Ag_2C_2 and not $C_2H_2Ag_2O$ as stated by other authorities.

It now remained to try its action upon ethylene. When 26 cc. of known ethylene were treated with an excess of ammoniacal silver chloride, only 0.2 cc. were absorbed, and repeated trials gave the same result; so that, although there is not absolute insolubility of ethylene, the method was admirable for its quickness and, of course, infinitely more accurate than the use of ammoniacal cuprous chloride.

Lastly the effect of the reagent upon known mixtures of pure acetylene and ethylene was tried. 29.2 cc. of ethylene and 37.3 cc. of acetylene were taken, and treated with the silver solution. The residue left corresponded closely with the volume of ethylene taken, thus showing conclusively that a mixture of the two gases may readily be separated by this method. Fractional percentages of ethylene might be lost and for such small amounts there seems nothing better than recourse to the gravimetric determination of the copper corresponding to the acetylene present, but this is not necessary for ordinary work.

[1] Lewes' "Acetylene," p. 154.

THE DETERMINATION OF SULPHUR IN IRON AND STEEL.

By William A. Noyes and L. Leslie Helmer.[1]

Received July 1, 1901.

ALTHOUGH very many methods for the determination of sulphur in iron have been proposed,[2] none of those in common use is altogether satisfactory. None of the evolution methods will give correct results with some irons, unless the evolved gases are led through a heated tube to convert organic compounds of sulphur into hydrogen sulphide.[3] The aqua regia method sometimes leaves sulphur in the residue[4] and the precipitation of barium sulphate in the presence of iron, which it usually involves, is always objectionable. The method which we propose obviates at least a part of these difficulties.

SOLUTION.

We tried at first various methods of solution, including solution in concentrated nitric acid and hydrochloric acid, as given by Blair in his "Chemical Analysis of Iron," in concentrated nitric acid with a little potassium chlorate toward the end of the solution; in hydrochloric acid and potassium chlorate; in bromine and water; and in dilute nitric acid with a little potassium bromide and an excess of potassium chlorate. The last two methods were finally adopted as the most satisfactory.

Solution in Bromine and Water.—The bromine must, of course, be free from sulphur. Ours was purified by mixing with a little dry sodium carbonate and distilling from a plain retort. Put 200 cc. of water and 8 cc. of bromine in a flask and add 5 grams of the iron or steel in portions, cooling after each addition. Solution takes place readily. When it is complete, boil for a moment to expel the slight excess of bromine. Filter, wash the residue, add to it some sodium carbonate and burn the filter in a platinum crucible, using an alcohol lamp, and completing the oxidation by the addition of some potassium nitrate. Dissolve the residue in water, filter, acidify with hydrochloric acid, add 5 cc. of barium chloride solution, digest till the precipitate settles readily and

[1] The work here described formed the basis of a thesis for the degree of Bachelor of Science at the Rose Polytechnic Institute. The preliminary work on the subject was done by Mr. Herbert F. Madison, of the class of 1900.

[2] See Bibliography by Brearley in *Chem. News*, **82**, 281 (1900).

[3] Phillips: This Journal, **17**, 891.

[4] Blair: This Journal, **19**, 114.

determine as usual.[1] Add *three-fifths* of the weight of barium sulphate found here to that obtained from the main solution. The main solution, containing ferric bromide, is to be precipitated as described below.

More sulphur is usually found in the residue by this process than by the solution in nitric acid and potassium chlorate, but it has the advantage that the solution can be filtered at once, while the solution in nitric acid clogs a filter so badly that evaporation to dryness is required.

2. *Solution in Nitric Acid, Potassium Bromide and Potassium Chlorate.*—Put into a flask 120 cc. of dilute nitric acid (sp. gr. 1.20, or 1 : 2 by volume) and 1 gram of potassium bromide. Add in portions, 5 grams of the iron mixed with 7 grams of potassium chlorate, cooling somewhat, if necessary. When the iron is dissolved, transfer to a flat porcelain dish and evaporate to dryness in such a manner that contact with the products of combustion of the gas is avoided. Dissolve the residue in concentrated hydrochloric acid, dilute, filter, and treat the residue as before, and the filtrate as directed below.

PRECIPITATION.

Put into a 500 cc. graduated flask 130 cc. of ammonia (10 per cent.), and add the solution obtained by either method above. Make the volume up to 500 cc., mix thoroughly by pouring back and forth into a dry beaker, and filter through a dry filter. The filtrate must, of course, be strongly alkaline. Take 300 cc. of the filtrate and evaporate, in a wide beaker, to 100 cc. During this evaporation contact with the products of combustion of illuminating gas must be avoided. We have used for the purpose a piece of stove-pipe flattened on one side and connected at one end with an elbow and upright piece to carry away the products of combustion. The hot steam plate of most iron and steel laboratories would be admirably adapted to this purpose. Add one drop of dilute hydrochloric acid (sp. gr. 1.12) and 10 cc. of barium chloride, digest hot till the precipitate settles quickly after stirring; filter, ignite and weigh as usual. The precipitate represents the amount of sulphur in 3 grams of the iron or steel.

To test the accuracy of the precipitation, seven determinations

[1] Dr. C. B. Dudley, who has kindly done some work with the bromine method, is of the opinion that the barium sulphate obtained from the residue requires purification by fusion with sodium carbonate, and it seems that this point requires further study.

were made with solutions containing known amounts of sulphur. For the first three a low sulphur steel was dissolved in hydrochloric acid, the solution boiled, filtered, and oxidized to ferric iron with bromine. Two blanks, made with quantities of this solution representing 5 grams of iron, gave respectively 0.0001 and 0.0004 gram barium sulphate.

The fourth and fifth determinations were made with a solution obtained by dissolving 5 grams of steel No. 1 in water and bromine. The mean value for the sulphur in this steel, neglecting the residue, had been found to be 0.027 per cent. The sixth and seventh determinations were made with 5 grams of iron No. 1, which contains, apart from the residue, 0.095 per cent. of sulphur. The extra sulphur for these experiments was added in the form of ferrous ammonium sulphate. The results are stated as percentages of the iron used, and indicate the accuracy to be expected in actual work, so far as this depends on the method of precipitation used.

Sample.	Sulphur present.	Sulphur found.
Sulphur-free iron + $Fe(NH_4)_2(SO_4)_2$.....	0.0056	0.0050
Sulphur-free iron + $Fe(NH_4)_2(SO_4)_2$.....	0.012	0.011
Sulphur-free iron + $Fe(NH_4)_2(SO_4)_2$.....	0.016	0.016
Steel No. 1 + $Fe(NH_4)_2(SO_4)_2$.....	0.129	0.129
Steel No. 1 + $Fe(NH_4)_2(SO_4)_2$.....	0.234	0.211
Iron No. 1 + $Fe(NH_4)_2(SO_4)_2$.....	0.490	0.500
Iron No. 1 + $Fe(NH_4)_2(SO_4)_2$.....	0.689	0.679

The advantages of this method of precipitation are that the precipitation is made with a solution free from iron, and that by the evaporation of the ammoniacal solution it becomes neutral, and by the addition of one drop of dilute hydrochloric acid a constant degree of acidity is secured. The results indicate that, even with very small amounts of sulphur, an accurate precipitation is secured in the presence of ammonium chloride or bromide.

To secure a uniform sample for use in testing the method, a considerable quantity of cast-iron drillings were ground to a fine powder in a heavy iron mill. Samples Nos. 1 and 2 were prepared in this way. Samples Nos. 3, 4, and 5 were ordinary drillings of iron used in making car wheels. Nos. 6 and 7 were samples of steel.

Determinations were made with sample No. 1 by Blair's gravimetric evolution method, using an alkaline solution of lead to

absorb the hydrogen sulphide evolved; and by Blair's aqua regia method, precipitating the sulphuric acid in the presence of the iron. As will be seen below, the evolution method gives less than one-half of the sulphur actually present in this iron. Whether the irregular and low results obtained by the aqua regia method are due to a failure to secure a complete oxidation of the sulphur during solution, or to imperfect precipitation of barium sulphate in the acid iron solution, can not be known with certainty, but the results of the aqua regia method, combined with our method of precipitation, point rather to the first explanation as the true one. The following are the results with iron No. 1:

Evolution method, Blair.	Aqua regia method, Blair.	
0.044	0.084	0.077
0.049	0.080	0.068
0.044	0.088	0.058
0.042	....	....

The following determinations were made with different methods of solution followed by precipitation of the iron with ammonia and determination of the sulphuric acid in an aliquot part of the filtrate.

Sample.	100 cc. H_2O, 35 cc. HCl (1.12), 7 grams $KClO_3$.	Con. HNO_3 with little con. HCl, Blair.	40 cc. con. HNO_3 with $\frac{1}{2}$ gram $KClO_3$.	100 cc. HNO_3 (1 20), 7 grams $KClO_3$.	200 cc. H_2O, 8 cc. Br.
Iron No. 1.	0.105	0.059	0.094	0.075	0.097
Iron No. 1.	0.041	0.074	0.097	0.084	0.095
Iron No. 1.	0.079	0.098	0.089	0.088	0.095
Iron No. 1.	0.077	0.031	0.087	....	....
Iron No. 1.	0.054	....	0.090	....	....

The results indicate that the use of concentrated nitric acid with the addition of a little potassium chlorate, when solution is nearly complete, or the use of bromine and water, give the most concordant and, probably, the most accurate results. The first of these methods is accompanied by the evolution of large volumes of nitrogen peroxide and requires considerable time. Solution in dilute nitric acid (sp. gr. 1.20) with potassium bromide and 7 grams of potassium chlorate is more rapid and gives satisfactory results.

In the following determinations the methods which have been described in detail were used. When the total sulphur is not given the solution was poured into the ammonia without previous

filtration. Where the total sulphur is given, the solution in bromine was filtered and the sulphur in the residue determined, while the solution in nitric acid was evaporated to dryness, the residue dissolved in concentrated hydrochloric acid, diluted, filtered, and the sulphur in the residue determined.

Sample.	200 cc. H_2O, 8 cc. Br.		120 cc. HNO_3 (1.20), 1 gram KBr, 7 grams $KClO_3$.	
	Soluble sulphur.	Total sulphur.	Soluble sulphur.	Total sulphur.
Iron No. 1.	0.097	....	0.084	....
Iron No. 1.	0.095	....	0.088	....
Iron No. 1.	0.095	....	0.091	....
Iron No. 1.	0.085	0.106	0.088	....
Iron No. 1.	0.093	0.117	0.093	0.120
Iron No. 1.	....	....	0.083	0.106
Iron No. 1.	....	....	0.099	0.116
Iron No. 1.	....	....	0.095	0.107
Iron No. 2.	0.068	0.091	0.088	0.099
Iron No. 2.	0.070	0.092	0.086	0.095
Iron No. 3.	0.129	0.155	0.157	0.159
Iron No. 3.	0.129	0.148	0.155	0.159
Iron No. 4.	0.113	0.144	0.142	0.149
Iron No. 4.	0.110	0.147	0.141	0.149
Iron No. 5.	0.075	0.095	0.083	0.095
Iron No. 5.	0.077	0.094	0.079	0.089
Steel No. 6.	0.026	....	....	....
Steel No. 6.	0.027	....	....	....
Steel No. 6.	0.026	....	....	....
Steel No. 6.	0.029	....	....	....
Steel No. 7.	0.018	0.029	0.019	0.022
Steel No. 7.	0.017	0.025	0.014	0.025

The sulphur of the residue, after solution in bromine and water, varies from 0.015 to 0.037 per cent. with an average of 0.023. The sulphur in the residue after solution in nitric acid, potassium bromide, and potassium chlorate, and evaporation, varies from 0.002 to 0.027 per cent. with an average of 0.012. With iron of a given character, the sulphur in the residue will probably be found nearly uniform, so that the original solution can be precipitated at once with ammonia, without previous filtration, and a constant correction for the sulphur of the residue applied. When this is done, the method becomes, we think, more rapid than any gravimetric method now in use.

TERRE HAUTE,
June 28, 1901.

THE SULPHOHALIDES OF LEAD.

By Victor Lenher.

Received June 19, 1901.

WHEN hydrogen sulphide is allowed to come in contact with a solution of lead chloride in hydrochloric acid, a brick-red precipitate appears. This precipitate consists of a combination of lead sulphide with the chloride. Hünefeld[1] prepared and studied this red substance and ascribed to it the formula $3PbS.2PbCl_2$. He treated a dilute lead acetate solution with hydrochloric acid and added hydrogen sulphide to the solution.

Reimsch[2] later studied the same substance. Parmentier[3] considers the formula $PbS.PbCl_2$ more nearly correct as it would be analogous to the oxychloride, $PbO.PbCl_2$.

It is also possible to prepare a yellowish red sulphochloride by digesting freshly precipitated lead sulphide with a solution of lead chloride.

Lead sulphochloride is a rather unstable body. Hot water gradually extracts lead chloride from it, leaving the sulphide. Excess of hydrogen sulphide completely converts it into the pure black sulphide.

Lead bromosulphide, like the chlorosulphide, is brick-red in color. Parmentier, who first obtained it, states that it can be prepared more readily than the chlorosulphide, but it is similar in its properties to the chlorosulphide. It corresponds to the formula $PbS.PbBr_2$.

Various attempts had been made to prepare the analogous iodosulphide of lead, but on account of the insolubility of lead iodide in dilute hydriodic acid, the attempts were fruitless until the author[4] tried the action of a solution of hydrogen sulphide on a solution of lead iodide in potassium iodide. This method of procedure gives the lead iodosulphide brick-red in color, having a more yellow shade than the other sulphohalides but similar in all respects to these derivatives. This brick-red lead iodosulphide corresponds to the formula $PbS.4PbI_2$. It is a very unstable compound.

[1] *J. prakt. Chem.*, **7**, 27.
[2] *Ibid.*, **13**, 130.
[3] *Compt. rend.*, **114**, 298.
[4] This Journal, **17**, 511.

While lead iodide is almost insoluble in dilute hydriodic acid, it dissolves readily in the stronger acid. When hydrogen sulphide gas is added to a solution of lead iodide in hydriodic acid, neither the sulphide nor the iodosulphide is obtained. If, however, an aqueous solution of hydrogen sulphide is added to the hydriodic acid solution of the iodide, yellow lead iodide is first precipitated by the dilution and appears as a fine crystalline precipitate. Further addition of hydrogen sulphide solution causes the conversion of the yellow iodide into the brick-red iodosulphide. This precipitate on analysis was found to correspond to the formula $PbS.4PbI_2$. We are therefore led to believe that whatever the method of preparation, the red iodosulphide of lead has always the same composition.

Thus far it has been impossible to obtain a lead fluorsulphide. The slight solubility of lead fluoride in water, and in the alkaline fluorides has thus far prevented its preparation. It has likewise been impossible to obtain a fluorsulphide by digesting lead fluoride with lead sulphide in a similar manner to that by which it is possible to prepare the chlorosulphide. Moreover, lead sulphide is insoluble in hydrofluoric acid while the other halogen acids readily dissolve the sulphide. Its preparation would appear improbable.

That these derivatives are possible under certain definite conditions and that these conditions must be adhered to, is evidenced by the fact that a too dilute solution of the lead salt in the halogen acid, or even a slight excess of hydrogen sulphide, causes the formation of pure black lead sulphide, which contains no halogen. On the other hand, since lead sulphide is soluble in the strong aqueous solutions of the halogen acids, it is impossible to prepare these compounds by means of the addition of hydrogen sulphide to the strong acid solutions. It is necessary that certain conditions be observed in order to make the existence of these compounds possible.

That such conditions are necessary can be shown in a very simple manner. Either precipitated lead sulphide or the natural sulphide, galena, dissolves readily in the strong aqueous halogen acids with evolution of hydrogen sulphide gas and the formation of the corresponding halide. With a strong halogen acid, hydrogen sulphide is liberated and when sufficient liquid is present, part of the gas remains in solution. The addition of water to

this solution gives, when proper conditions are established, the brick-red compound which might be considered as an intermediate product between the halide and the sulphide.

The three sulphohalides of lead are all readily prepared by this means. The bromosulphide is the most stable of the compounds and it can be prepared in a very striking manner by treating 2 to 3 grams of lead sulphide or galena with 10 to 15 cc. of strong hydrobromic acid, and diluting with a large volume of water. The acid should be allowed to act until hydrogen sulphide is freely evolved. The solution will retain sufficient gas so that when a liter of water is quicky added, the brick-red bromosulphide appears.

Hydrochloric and hydriodic acid solutions of galena, when freshly prepared and quickly diluted, behave in a similar manner. With the hydrochloric acid solution the conditions are better obtained when more acid is present than above noted for hydrobromic. When this solution is diluted with water, the bright red chlorosulphide appears, sometimes preceded by the white chloride. Excess of water invariably causes the chlorosulphide to change to the black lead sulphide, which is the final product. The formation of the bromosulphide by this method makes an extremely beautiful experiment; the simple addition of water to a freshly prepared solution of galena in hydrobromic acid gives bright yellow bromide which almost instantly changes to a bright red. On further diluting and allowing to stand, the black sulphide is obtained. These changes seem to indicate that the formation of these compounds is due to certain definite relations between the halide and hydrogen sulphide in a solution of the corresponding halogen acid.

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A MODIFICATION OF THE SULPHURIC ACID TEST FOR FORMALDEHYDE IN MILK.

BY A. GUSTAV LUEBERT.

Received July 10, 1901.

WHILE estimating nitrogen, by the Kjeldahl-Gunning method, in a number of samples of milk which had been preserved by the addition of a small quantity of formaldehyde, a peculiar violet coloration of the potassium sulphate crystals and sulphuric acid, surrounding them, was noticed. Especially was

this true when the milk was added to the potassium sulphate and the sulphuric acid carefully poured down the side of the digestion flask, so that the liquids did not immediately mix. The violet or reddish-violet color appeared only in those samples of milk which contained the formaldehyde; in all others caramelization ensued at once, the crystals and the liquid becoming first brown and then black.

A number of tests were made upon milk to which formaldehyde had been added, and in each case the preservative seemed to retard the oxidizing action of sulphuric acid, causing the violet coloration to appear and preventing the usual caramelization of the milk. In none of the samples where formaldehyde was added was a negative result obtained.

These trials led to the adoption of the following method for the detection of formaldehyde in samples of milk: 5 grams of coarsely powdered potassium sulphate are placed in a 100 cc. flask, 5 cc. of the suspected milk distributed over it by means of a pipette and 10 cc. of sulphuric acid (sp. gr. 1.84), carefully poured down the side of the flask. It is now allowed to stand quietly until the color develops. If formaldehyde is present the violet coloration of the potassium sulphate takes place in a few minutes, the color gradually dispersing through the entire liquid. If no formaldehyde be present the liquid will at once assume a brown color, rapidly changing to black. Milk which has stood for several hours previous to testing gives the reaction even more rapidly than a fresh sample.

This test is sensitive to a dilution of at least one part formaldehyde in 250,000 parts of milk.

NEW BOOKS.

QUALITATIVE ANALYSIS: A GUIDE IN QUALITATIVE WORK, WITH DATA FOR ANALYTICAL OPERATIONS AND LABORATORY METHODS IN INORGANIC CHEMISTRY. BY ALBERT B. PRESCOTT AND OTIS C. JOHNSON. Fifth Revised and Enlarged Edition, Entirely Rewritten. New York: D. Van Nostrand Co. 1901. xi + 420 pp. Price, $3.50.

So much new matter has been added to this edition of Prescott and Johnson's manual that it is almost a new work. The subject matter has been enlarged over the former edition by fully one-half, and the size of the book increased 100 pages. The introduction of a section on "Solution and Ionization" will aid teachers in making the subject clear to beginners. Much descriptive

chemistry has been introduced throughout the book, and while at first sight this may seem a little foreign to a work of this class, it must be remembered that not only will this serve the student as a review of elementary chemistry, but the knowledge given of the physical properties, such as the color and solubility of the various salts, will greatly aid him in forming his opinion as to the composition of a substance. The descriptive, as well as the analytical, matter is well arranged under a series of systematic headings, and the former is separated from the latter by the use of small type. Reactions are used throughout the book to show the changes that take place in precipitation, solution, etc., and the schemes and tables are carefully explained. The rare elements receive their share of attention, and the book is brought well up to date in the introduction of new tests. Abundant reference to the literature of chemistry makes it easy for those so inclined to go deeper into any part of the subject. The book is well printed and neatly bound. In the reviewer's opinion the manual is the most complete work on the subject printed in English, and it deserves to rank with the standard German manual of Fresenius. Whether the teacher can use it in the classroom is for each individual to decide for himself, but the book should certainly be in the library of every teacher of chemistry, and may well be in that of every professional chemist and student of chemistry.

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